

Pyrite etc

1912

292

[FROM THE AMERICAN JOURNAL OF SCIENCE, VOL. XXXIII, March, 1912.]

W. F. FOSHAG

Division of Mineralogy

THE MINERAL SULPHIDES OF IRON

By E. T. ALLEN, J. L. CRENSHAW

and JOHN JOHNSON

WITH CRYSTALLOGRAPHIC STUDY

By ESPER S. LARSEN



THE
AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XX.—*The Mineral Sulphides of Iron*, by E. T. ALLEN,
J. L. CRENSHAW, and JOHN JOHNSTON; *with Crystallo-*
graphic Study, by ESPER S. LARSEN.

INTRODUCTION.

Application of Chemistry to the problems of ore deposition.—The problems of ore deposition have claimed the attention of geologists for a long time, both for economic and for scientific reasons. The difficult questions as to the origin of ores and the conditions of their genesis have been zealously studied, and with notable success; yet despite the great advances which have been made, no one will question that the scarcity of chemical data has been a serious drawback in the development of the subject. A laboratory investigation of some phases of it involves, indeed, difficulties which are still to be surmounted, but the problems of the temperature ranges within which the minerals have crystallized, the composition of the solutions from which they have come, and the agencies which have precipitated them are in general not only within the bounds of chemical possibility but within the limits of present day methods.

The sulphides of iron.—The sulphide ores from a chemical view-point are of very great interest, and geologically, they are of high importance. The sulphides of iron, in particular, frequently carry paying quantities of gold and nickel, and when themselves barren, are so frequently associated with other valuable ores as to hold a place of unusual significance in a general consideration of the subject of ore deposition. The chemical knowledge of these substances is still very meager. Syntheses of pyrite and pyrrhotite were made long ago by

Wöhler, Rammelsberg and others, but for the most part by methods which throw little light on their formation in nature.*

Method of study.—In the investigation of this subject the synthetic method has been largely followed, while the most significant properties, reactions and relations of the substances have been studied. Some of the material will be chiefly of chemical interest, but the effort has been made to give special attention to the chemical geology involved and to this end the authors have consulted frequently with several eminent geologists who are specialists in this field. The experience and suggestions of these scientists have been of great value and will be duly acknowledged in the proper place. No optical studies were of course possible on opaque minerals, but crystallographic measurements were made and such microscopic studies as the character of the material admitted of.

I. The disulphides (FeS_2) Pyrite and Marcasite.

Two disulphides of iron are known—pyrite, hard, lustrous, brassy-yellow, of sp. gr. 5.027† at 25°, and crystallizing in the regular system; and marcasite, yellowish grey in color, a little softer than pyrite, of sp. gr. 4.887† at 25° and crystallizing in the orthorhombic system. Both minerals are almost insoluble in hot hydrochloric and dilute sulphuric acids, and both are decomposed by nitric acid. Both are slowly oxidized by free oxygen, the products being, according to conditions, sulphur dioxide and ferrous sulphate, or sulphuric acid and ferrous or ferric sulphate,—sometimes, in fact, sulphuric acid and ferric hydroxide. The conditions have not been investigated completely, though certain definite statements can be made at the present time. In a closed vessel containing air, i. e., with an *excess of sulphide*, the products are sulphur dioxide and ferrous sulphate. When the minerals are heated to 100° in air or ground dry in a mortar, these are the *first* products at least. The sulphur dioxide changes pretty readily, of course, to sulphuric acid. When kept in contact with air and moisture at 75° most of the iron takes the form of ferric hydroxide. Many oxidizing agents, important among which, from a geological standpoint, are ferric sulphate and copper sulphate solutions, change pyrite and marcasite into ferrous sulphate, sulphur and sulphuric acid. In nitric acid of 1.4 sp. gr., powdered pyrite dissolves completely, while marcasite separates sulphur.‡ Both minerals are so nearly

* An exception should be made of the excellent work of Senarmont, Ann. Ch. Phys., xxxii, 129, 1851.

† These specific gravities were determined on very pure natural minerals, the analyses of which are given on p. 177.

‡ Brush and Penfield's Determinative Mineralogy, 15th ed., p. 252.

insoluble in water that some statements* regarding their solubility, found in the literature, could only have been made on the basis of experiments in which atmospheric oxygen was not excluded. In all these instances the two minerals behave much alike, though marcasite is always more soluble in any medium and is more readily changed by oxidizing agents.

Formation of iron disulphide in nature.—Geologists appear pretty well agreed that pyrite sometimes crystallizes direct from rock magmas. Pyrite, however, in the great majority of cases, and marcasite in all cases, crystallize from water solutions, though the nature of the process is purely a matter of conjecture. Here a general line of division should be made between the products of *hot* and the products of *cold* solutions. The pyrite of *deep* veins, metamorphic contacts and hot springs, as well as magmas, has been formed by hot solutions, and such solutions never contain strong mineral acids, but are generally if not always alkaline. The pyrite and marcasite of surface veins, on the other hand, are formed from cold solutions which often contain considerable sulphuric acid. We shall find cogent reasons for the conclusion that the chemistry of these two processes is similar, but first let us consider the formation of iron disulphide from surface solutions. Here the geologic hypothesis is that both minerals have been formed by the “reduction” of ferrous sulphate through the agency of organic matter, and indeed, the frequent occurrence of pyrite in coal and its occasional formation on wood gives plausibility to this view. It is plain that the soluble sulphate of iron could not be changed by *simple reduction* to the disulphide, though one might imagine such a reaction as the following equation imperfectly represents:

$7C$ (vegetable matter) $+ 4FeSO_4 = 2FeCO_3 + 2FeS_2 + 5CO_2$.
Some experiments have been tried in this laboratory in the hope of “reducing” ferrous sulphate with organic matter, but the results have not been promising. The action of starch and glucose on aqueous solutions at 300° was either slight or nil. On the other hand, the possibilities of hydrogen sulphide are suggestive. Pyrite and marcasite are very often found with simpler sulphides,—those of lead and zinc for example, which may be easily formed by the action of hydrogen sulphide; and furthermore, hydrogen sulphide is a substance widely distributed in nature. Without denying that carbonaceous substances may in some instances be directly active in the formation of pyrite and marcasite, we will proceed to show that both minerals may be formed through the agency of hydrogen sulphide, and under conditions which doubtless prevail commonly in nature.

* See Doelter, *Tschermak's Min. Petr. Mitt.*, N. F. xi, 322, 1890; *Neues Jahrb.*, ii, 273, 1894.

Synthesis of iron disulphide.—Apparatus.—All the experiments on the synthesis of pyrite and marcasite were done in

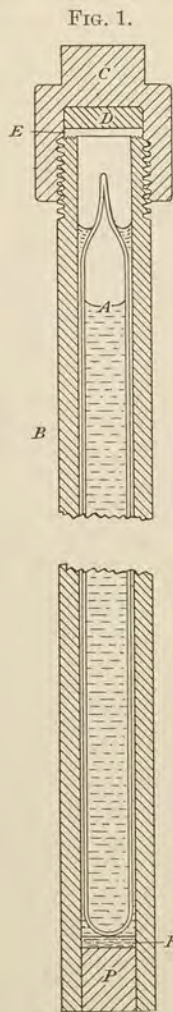


FIG. 1. Bomb used in heating sealed tubes.

sealed tubes, enclosed in steel bombs and heated in resistance furnaces. Several kinds of glass were tried for the tubes, all of which were naturally more or less attacked. The Jena combustion glass and so-called "durax" glass were the only kinds which were found to stand satisfactorily the action of water solutions at the higher temperatures (up to 350°), and even these are pretty rapidly attacked by alkaline solutions. To prevent bursting, the glass tubes were enclosed in heavy steel bombs (see fig. 1), about 80 cm in length by 25 mm inside and 43 mm outside diameter, having thus a thickness of nearly a centimeter. These bombs were closed at one end by an iron plug, P , which was welded in. The other end was threaded on the outside and closed with a cap. To insure a tight joint, three concentric grooves about 1 mm deep were cut on the open end of the bomb. On this was laid a copper disc, E , 3 mm thick, on which was placed a steel disc, D , 1 cm thick. The cap was then screwed down by means of a long steel lever. The steel disc was used to prevent the shearing of the copper disc in screwing down the cap. The joint was lubricated with oil and graphite. The glass tubes were put into the bombs and water was added before closing the latter, so that the pressure on the inside of the glass tubes would be compensated. These bombs will hold satisfactorily up to temperatures of 400° .

Furnaces.—The furnaces in which the bombs were heated were electric resistance furnaces, the coils of which were of nickel wire 0.8 mm in diameter, wound on a sheet-iron tube 5 cm in diameter, which was first wrapped with asbestos paper. The tube and coil were surrounded by another sheet-iron cylinder 15 cm in diameter. The space between the two was filled with light magnesium oxide. Caps, also of sheet-iron, fitted tightly over both ends of the outside tube, leaving at the upper end (the furnaces were set in an inclined position) a space about

6^{cm} long for the head of the bomb. A hole about 6^{mm} in diameter through the lower cap admitted the thermo-element. The variation in temperature along the outer wall of the bomb, from a point about 5^{cm} from the lower end to another 20^{cm} farther up, was only about 5°, which is within the error of the direct-reading galvanometer used. This instrument was calibrated within that degree of accuracy, but as none of the temperatures involved had reference to any critical point, it was not considered worth while to measure more accurately.

The action of hydrogen sulphide on ferric salts.—The first action of hydrogen sulphide on ferric salts is, of course, the immediate reduction of the latter and the simultaneous precipitation of sulphur: $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{S} = 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{S}$. No further action has hitherto been noticed, but in a closed vessel where the hydrogen sulphide is prevented from oxidation or escape, a second reaction proceeds, viz: $\text{FeSO}_4 + \text{S} + \text{H}_2\text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$. At room temperatures, the velocity of this change is very slow, but at 200° it is relatively rapid. The following data prove beyond question the nature of this latter reaction:

3 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with 0.17 g. H_2SO_4 , 0.75 g. sulphur and 100^{cc} water saturated at 0° with H_2S , were sealed up in a glass tube and heated about 2 days at 200°. The product was purified by washing first with water, then digesting with ammonium sulphide to remove excess of sulphur, washing again with water, boiling out with 20 per cent hydrochloric acid, and finally washing in an atmosphere of carbon dioxide and drying in vacuo.

Analysis: Product taken, 0.5044 g. Fe_2O_3 found, 0.3346 g.

	Found	Cal. for FeS_2
Fe	46.44%	46.56%

Another product was formed by heating at 100° for six days the following system: 5 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g. S, 0.17 g. H_2SO_4 , and 100^{cc} water saturated at 0° with H_2S . The product was purified in a way similar to the above.

Analysis: Product taken, 0.5003 g. BaSO_4 found, 1.9598 g.
 “ “ 0.5006 g. Fe_2O_3 “ 0.3295 g.

	Found	Cal. for FeS_2
Fe	46.06%	46.56%
S	53.81	53.44
	<hr/> 99.87	<hr/> 100.00

Both these products were similar to natural marcasite in color and luster. Their crystalline nature was very obvious to the unaided eye, though the crystals were small.

Methods of distinguishing pyrite from marcasite.—To distinguish between the disulphides pyrite and marcasite, two methods were employed.

1. Crystals were prepared large enough for goniometric measurement. When hydrogen sulphide and sulphur act directly on a solution of ferrous sulphate, the crystals are in general

FIG. 2.

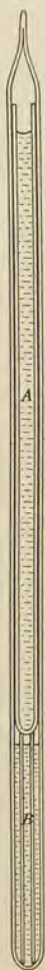


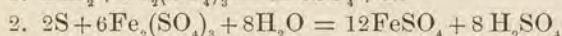
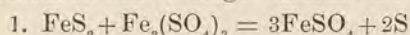
FIG. 2. Apparatus for the slow formation of crystals of iron disulphide.

minute. They increase in size with rise in temperature and several other conditions. One of the most important of these is slow formation. This can be brought about by a simple device (fig. 2). Into a glass tube of about 18^{mm} inside diameter and 65^{cm} in length, is poured through a funnel about 7–10 g. of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) dissolved in 30^{cc} water. The ferric salt is contained in another smaller tube which slips into the larger. The small tube has a diameter of 15^{mm} outside and a length of 45^{cm}. It is supported above the thiosulphate solution by a piece of glass tubing a little longer than the depth of the liquid. When the outer tube is sealed, the whole is heated in a bomb as usual. At a temperature of 200°, hydrogen sulphide is slowly generated from the thiosulphate solution, according to the following equation: $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$. By the action of the gas on the ferric salt solution, crystals of measurable size have been repeatedly formed. This scheme, however, could not be satisfactorily used in studying the influence of various conditions on the crystal form. Obviously, not all the crystals of any product could be measured, and it was, of course, a thankless if not impossible task to identify all of them microscopically. Therefore, a quantitative estimation of the two minerals in mixtures could not be made. Besides, the method of synthesis is very slow.

2. Stokes's oxidation method. Some years ago, a chemical method for distinguishing between pyrite and marcasite was worked out by H. N. Stokes.* Since free use of this method has been made, it will be necessary to explain it in some detail. It

* H. N. Stokes, Bull. U. S. Geol. Survey, 186.

depends on the difference in behavior between the two minerals toward a solution of ferric sulphate. In both cases the sulphide which is used in *excess* reduces the ferric salt completely to ferrous sulphate, while the mineral itself is oxidized to ferrous sulphate, sulphuric acid and free sulphur. It is in the relative quantities of the products that the difference between pyrite and marcasite shows itself. The reaction may be represented in two stages as follows:



In that portion of the sulphide which takes part in the reaction, the percentage of the sulphur which is oxidized to sulphuric acid depends on conditions, but, *ceteris paribus*, the quantity is much greater for pyrite than for marcasite. In order to distinguish between the two it is therefore necessary to determine what percentage of the sulphur is oxidized to sulphuric acid. Stokes found it most advantageous to use a standard solution (ferric ammonium alum) containing 1 g. of iron and 4.0 g.* free sulphuric acid per liter, and to operate at the boiling temperature. Under these conditions, he found that 60 per cent of the sulphur in pyrite was oxidized, and only 18 per cent of the sulphur in marcasite. Instead of determining *directly* the quantity of free sulphur or sulphuric acid formed in the reaction, Stokes measured the increase in the concentration of ferrous iron in solution. By stoichiometrical calculation, for the details of which the original paper must be consulted, he derived the formula, $p = \frac{8.33b}{c-a} - 25$, where p is the percentage of sulphur in the reacting sulphide which is oxidized to sulphuric acid, b the *ferrous* iron, c the *total* iron in the solution at the end of the operation, and a the total iron in the *original* solution. There is one point on which Stokes does not express a perfectly clear view, viz: whether the solution at the end of the oxidation should contain any ferric iron or not. As a matter of fact, the reaction, when successful, proceeds to completion, so that all the iron at the end of the operation is ferrous; b and c are consequently identical, and the formula may therefore be simplified to $p = \frac{8.33b}{b-a} - 25$.

Stokes determined the ferrous iron by direct titration with permanganate. Afterwards he reduced the solution and titrated again so as to determine the *total* iron, ferrous and ferric. This reduction and subsequent titration are evidently superfluous. The process has been improved in several other

* This is our interpretation of Stokes's statement: "16^{cm}3 of 25 per cent sulphuric acid."

details also. The sulphide has to be very carefully purified. Obviously, any other product which could reduce the solution, or anything like ferrous sulphate or ferric hydroxide which could in any way increase the concentration of the ferrous iron, would interfere with correct conclusions. In the main, Stokes' procedure has been followed, though a new apparatus for

FIG. 3.

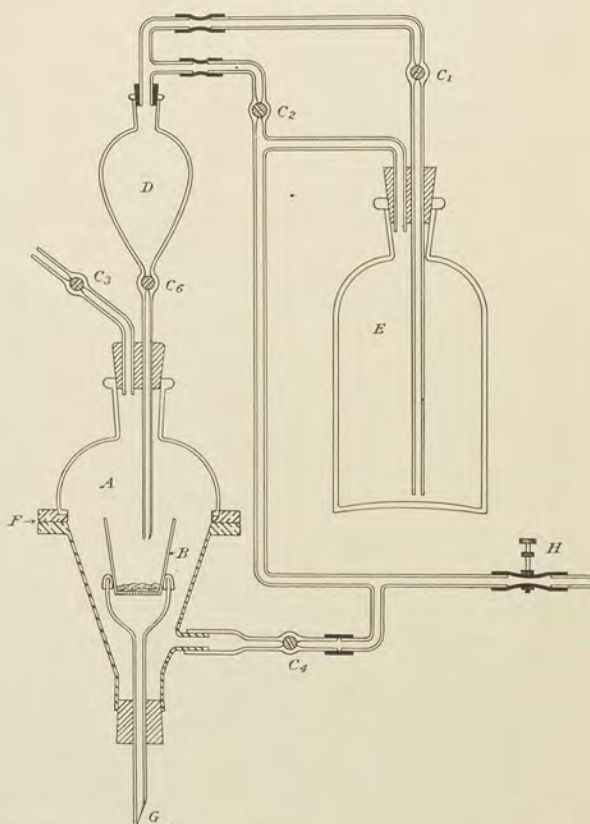


FIG. 3. Apparatus for washing substances out of contact with air.

washing substances out of contact with the air has been devised and used. This apparatus, which is shown in the adjoining figure (fig. 3), has proved of very general utility and convenience. *A* consists of two parts, the lower of brass, the upper of glass cemented into a brass ring. *F* is a ground joint between this ring and another similar ring soldered to

the lower half of the apparatus. In use, this joint is greased with vaseline and the rings are held in place by two spring clamps which are not shown in the figure. The two vessels *D* and *E* are used to contain, respectively, hydrochloric acid and boiled water cooled in carbon dioxide, with which two liquids the ground sulphide in *B* is successively washed. The pressure of the carbon dioxide which enters the apparatus at *H* is sufficient to drive either liquid over into *B* when the proper stop-cocks are opened. *G* opens into a filter flask filled nearly full of water, connected with the water pump. Suction is carefully regulated by a pinch-cock. The apparatus is successively evacuated by the pump and filled with carbon dioxide before using. In drying the material in the vacuum desiccator, instead of using the water pump as Stokes did, we have evacuated by an oil or mercury pump to a fraction of a millimeter. At the end of a half hour the sulphide is not dry but it does not contain enough water to affect the result essentially. In the determination of the ferrous iron, we have employed a weight burette instead of a volume burette.

Results with natural pyrite and marcasite.—The minerals employed were pyrite from Elba* and marcasite from Joplin, Mo. They were purified with great care and then analyzed.† The only impurities found were small quantities of silica and a minute trace of copper in the marcasite.

	Marcasite	Pyrite	Cal. for FeS ₂
Fe	46.53	46.49	46.56
S	53.30	53.49	53.44
SiO ₂	.20	.04	
	<hr/> 100.03	<hr/> 100.02	<hr/> 100.00

The oxidation coefficients obtained by us were 56 for pyrite and 14 for marcasite, while Stokes found 60 and 18 respectively. The differences have not been entirely accounted for, though we have taken somewhat greater precautions in our work. However, and this is the point to be emphasized, the results of each are probably consistent among themselves.

Determination of the relative quantities of pyrite and marcasite in mixtures.—By grinding together the two minerals in different proportions and then determining the oxidation number for the mixture, Stokes constructed a curve repre-

*In some of the later experiments, a pyrite from Leadville, Col., containing 0.1 per cent copper, was used.

†For the method of analysis, see Allen and Johnston, Zs. anorg. Chem., lxi, 102, 1911.

senting the oxidation coefficients for all possible mixtures. His curve had the form of a eutectic curve with the lowest point at ten per cent, pyrite having an oxidation coefficient of about 15. Fig. 4 shows the curve which we obtained for mixtures of pyrite and marcasite. Careful experiment failed to reveal any mixture which gave a lower oxidation coefficient than pure marcasite. The difficulty of determining accurately the composition of an unknown mixture, by a measurement of

FIG. 4.

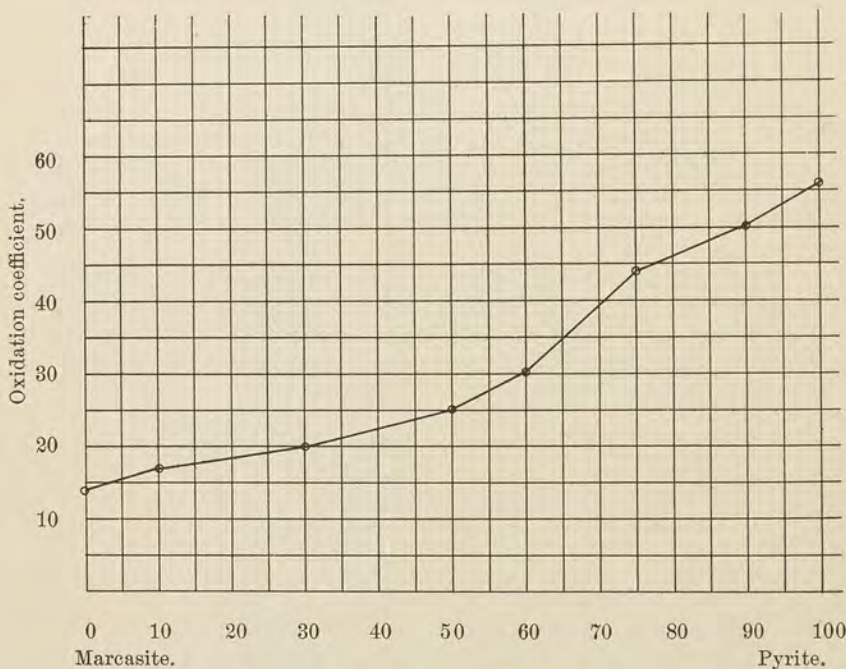


FIG. 4. Curve showing the oxidation coefficients for mixtures of pyrite and marcasite.

the oxidation coefficient, is obvious from the form of the curve; indeed, differences of two to three per cent (of the weight of the mixture) were usually found in duplicate determinations. Yet, though we cannot confirm the statement of Stokes regarding the accuracy of the method, we have found it of great value in studying synthetic products of iron disulphide, the mineral composition of which must otherwise have remained unknown, and have been thus enabled to work out the essential conditions which govern the formation of pyrite or marca-

site. Of course, the method only applies where the substance contains no other reducing agent than pyrite and marcasite. If, therefore, we had present another crystal form of FeS_2 , the results would be unreliable. Although both pyrite and marcasite have been repeatedly detected by the microscope in the synthetic products, no evidence of another form has come to light. It is possible that in some instances (which will be pointed out in the proper place) amorphous FeS_2 may have been present. In most cases, however, the crystalline structure was so apparent even to the unaided eye that the presence of any amorphous material was quite unlikely, and this conclusion was only confirmed by the microscopic study.

Marcasite.—Marcasite is the principal product when hydrogen sulphide acts directly on ferric sulphate at 200° .

Exp. 1.5 g. $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 100°C water saturated at room temperature with hydrogen sulphide, was sealed up and heated in a bomb for several days at 200° . To insure a sufficient quantity of the product for experiment, three tubes were thus heated under the same conditions. The product was removed, ground fine, purified, and the oxidation number determined. It was found to be 23.6, corresponding to about 43 per cent pyrite.

Influence of free acid on the proportion of marcasite.—The equation $\text{H}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 = \text{S} + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$ shows that sulphuric acid is a product of the reaction in which the marcasite forms, and its concentration evidently increases as the reaction proceeds. It was, therefore, a plausible hypothesis that the concentration of acid influences the crystal form; it seemed possible that the pyrite might have formed in the earlier stages of the process, when the acid was weaker. If this view were correct, a greater initial concentration of acid should result in more marcasite. The hypothesis is proved correct as shown by the results collated in the adjoining table.

TABLE I.

The effect of free H_2SO_4 on the formation of marcasite at 200° .

Taken			Found	
$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Water saturated with H_2S	Free H_2SO_4^*	Oxidation number	Per cent pyrite
5 g.	100 cc	0.50 g.	23.6	43.
5 g.	100 cc	0.57 g.	18.9	25.
5 g.	100 cc	0.78 g.	17.0	10.0
5 g.	100 cc	1.18 g.	16.5	7.5

* This includes the acid formed in reduction of the ferric iron by hydrogen sulphide.

TABLE II.

Effect of temperature on the formation of marcasite.

Temperature	Taken				Found	
	FeSO ₄ . 7 H ₂ O	Sulphur	Free H ₂ SO ₄	Water saturated with H ₂ S at 0°	Oxidation number	Percent pyrite
300°	5 g.	0.5 g.	0.17 g.	100 cc	29.0	57.5
300°	5 g.	0.5 g.	0.17 g.	100 cc	28.4	56.5
200°	5 g.	0.5 g.	0.17 g.	100 cc	20.7	32.0
100°	5 g.	0.5 g.	0.17 g.	100 cc	16.	6.0
100°	5 g.	0.5 g.	0.17 g.	100 cc	17.2	10.0

Table II shows the influence of temperature on the reaction. Here ferrous sulphate and sulphur, the products of the action of hydrogen sulphide on ferric sulphate, were taken. The quantities of acid used, by inadvertence, were considerably less than intended, but the evidence shows the influence of temperature very plainly. The higher the temperature the greater is the quantity of pyrite formed. A word is here needed on the question of the formation temperature. The furnace was first heated to the required temperature, then the cold bomb containing the tube was introduced. Obviously, the reaction could not take place entirely at one temperature. At the lower temperatures, however, the reaction is very slow, so that the time required for the bomb to reach the temperature of the furnace is not important. When the bombs were heated to 300°, many hours were required to reach the maximum temperature. It would not be worth while, after having shown that the two variables, temperature and acid concentration, both influence the product of this reaction, to study the problem in great detail, but it is interesting to note that the reaction will proceed at ordinary temperatures, and also that pure marcasite may be obtained by a proper combination of the two variables. Thus at 100° the precipitate formed from a solution containing 1.18 per cent of free sulphuric acid gives the oxidation coefficient 14.5 and is therefore pure marcasite. From 2 liters of a solution which contained 3 per cent of hydrous ferrous sulphate and 0.15 per cent of free sulphuric acid, 1 gr. of precipitate was obtained at room temperature in about three weeks. Unfortunately, there was an accident in the determination of the oxidation coefficient of this product, but we can state that it contained less than 10 per cent of pyrite. For every temperature there appears to be a quantity of acid which inhibits the reaction:

$\text{FeSO}_4 + \text{H}_2\text{S} + \text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$. The quantity is smaller the lower the temperature. It appears to bear no relation to the solubility of the sulphide, for at room temperature this quantity is only a small fraction of 1 per cent. At 200° it lies between 3.5 per cent and 5 per cent; at least this is true for periods of a few weeks.

Crystals of marcasite.—Measurable crystals of marcasite were obtained by the slow action of hydrogen sulphide on ferric sulphate or chloride at several temperatures up to 300° (see p. 174). The general problem of making measurable crystals is one of the most troublesome in synthetic mineralogy. As yet we have no light on the means of controlling the number of nuclei which form in the process of crystallization. In general, the more soluble minerals are obtained in larger crystals. Likewise, larger crystals are obtained from a medium in which they are more soluble. In preparing well-formed marcasite crystals, some unaccountable failures were met with, though generally the products obtained by the method previously described contained a number of crystals which were measurable. The marcasite crystals were like the natural mineral in color and luster and the axial ratio deduced from the angular measurements was $a:b:c = 0.7646:1:1.2176$ as compared with $0.7580:1:1.2122$ for natural marcasite (Goldschmidt). The striations which marked the crystals agreed with orthorhombic and not with regular symmetry (see III, Crystallographic Study).

*Formation of pyrite.**—While the product of the action of sulphur and hydrogen sulphide on ferrous salts is largely marcasite, the percentage increasing with the quantity of free acid present, pyrite is the principal product where the solution remains neutral or but slightly acid.

Action of hydrogen sulphide on ferric hydroxide.—Freshly precipitated ferric hydroxide is instantly blackened by hydrogen sulphide. The product is a mixture of ferrous sulphide and sulphur, as shown by the following. Freshly precipitated ferric hydroxide was washed free of soluble salts, suspended in water and treated for some time with hydrogen sulphide. A portion of the black amorphous precipitate dissolved in cold dilute acid with evolution of hydrogen sulphide, leaving a residue of amorphous sulphur. Another portion was first digested with ammonium sulphide solution. After filtering

* For former syntheses of pyrite, see Wöhler (Ann., xvii, 260, 1836). Wöhler heated an intimate mixture of Fe_2O_3 , S, and NH_4Cl till the NH_4Cl was sublimed. He obtained some small brass yellow tetrahedra and octahedra. Senarmont (loc. cit.) obtained FeS_2 by heating ferrous salt solutions with alkaline polysulphides. Geitner (Ann. 129, 350, 1864) heated metallic iron with a solution of sulphur dioxide to about 200° . His product may have been marcasite. See also Doelter (Zs. Kryst., xi, 30, 1886).

and washing out the excess of reagent, the black residue dissolved without leaving any sulphur behind. The product therefore must have contained free sulphur and could not have been ferric sulphide, Fe_2S_3 , though the latter, according to Gedel,* decomposes with dilute acid, giving the same products as the above mixture. A product made by the action of hydrogen sulphide on ferric hydroxide was washed into a glass tube with about 100^{cc} water, saturated with hydrogen sulphide at room temperature, sealed and heated at 140° for seven days. The solution when cooled and opened still smelled strongly of hydrogen sulphide. The product had become quite dense and had a yellowish grey color. It was boiled in hydrochloric acid for some time to dissolve any unchanged ferric hydroxide, or ferrous sulphide, and further purified as usual. The oxidation number was 49, corresponding to 87 per cent of pyrite. The work was repeated with ferric hydroxide† which had been dried at 100° to make it easier to handle. It proved, however, much less susceptible to hydrogen sulphide. It had to be heated repeatedly at 140° with saturated hydrogen sulphide water before the color of the oxide of iron had disappeared entirely. After purification, the product gave the oxidation number 50·4, corresponding to 90 per cent pyrite.

Action of sulphur on pyrrhotite in the presence of a solvent.—The formation of pyrite, just described, is evidently a result of the direct union of sulphur and ferrous sulphide, the first product of the reaction. The hydrogen sulphide water probably acts as a weak solvent. Similarly, the marcasite may be regarded as a product of the addition of sulphur to ferrous sulphide, which forms gradually from solution. The formation of pyrite by the action of sulphur on crystalline pyrrhotite, the relation of which to ferrous sulphide will be shown farther on, proves conclusively that, at a given temperature, it is not the exact nature of the solid phase which reacts with the sulphur, but the composition of the solution in which it forms, that determines whether the product shall be pyrite or marcasite. 2·2 g. pyrrhotite prepared in the laboratory, and 0·8 g. of sulphur were put into a glass tube, to which was added a solution of 0·1 g. of sodium bicarbonate in 100^{cc} water. Before sealing the tube, the solution was partially saturated with hydrogen sulphide. In composition this solution was similar to that of a warm "sulphur" spring, and it served as a solvent for the sulphur, which was gradually absorbed by the pyrrhotite. The tube and its contents were heated for two months at 70°. The product at the end of that time still contained sulphur and undecomposed pyrrhotite. To remove the latter it was boiled

* Jour. für Gasbel., xlviii., pp. 400 and 428, 1905.

† According to Gedel (loc. cit.), $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is thus obtained.

for a long time with 20 per cent hydrochloric acid. The residue was dense and brassy-yellow. It was finely ground, purified as usual, and tested by Stokes's method. It gave an oxidation number of 55.1, which corresponds to pure pyrite within the limits of error of the method. To make sure that no mistake had been made in this test, some pure natural pyrite was compared the next day with the same ferric sulphate solution. 100^{cc} of the sulphate solution, after it had been reduced with the synthetic pyrite, required 42.51 g. of permanganate solution. 100^{cc} which had been reduced by natural pyrite took 42.56 g. of the permanganate.

The action of sulphur on pyrrhotite was tried again at 300°, where the reaction was of course much more rapid than at 70°.

Into the tube were put 5 g. powdered pyrrhotite, 1.75 g. sulphur, 0.2 g. NaHCO₃, and 100^{cc} water partially saturated with H₂S. The tube was heated four days at 300°. The oxidation number of the purified product was 52.0, corresponding to about 95 per cent pyrite. It is possible that these products contained a very little undecomposed pyrrhotite or perhaps amorphous FeS₂, both of which would have undoubtedly had a similar effect as marcasite in lowering the oxidation number.

TABLE III.

The oxidation numbers of FeS₂ formed from alkali polysulphide solution.

Time	Water	FeSO ₄ . 7H ₂ O	Na ₂ S ₂	Sulphur	Temperature	Oxidation number	Py- rite
3 days	100 ^{cc}	5 g.	plain excess	0.75 g.	300°	54	97%
5 days	100 ^{cc}	3 g.	plain excess	.75 g.	200°	40.5	71%
7 days	100 ^{cc}	3 g.	plain excess	.75 g.	100°	26	51%

The action of alkali polysulphides on ferrous salts.—Senarmont* in 1851 showed by analysis that the product of the action of alkali polysulphides on ferrous salts at 180° is FeS₂. The question of the crystal form was not investigated. The black amorphous precipitate† which is obtained at room temperature by the above reaction appears to be a mixture of sulphur and ferrous sulphide, at least it decomposes with dilute acids, giving a residue of amorphous sulphur, while hydrogen sulphide escapes. On heating, disulphide of iron gradually

* Loc. cit.

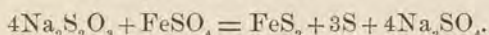
† Gedel (loc. cit.) claims that this precipitate is Fe₂S₃.

forms, though some of the black precipitate is still unchanged after it has been heated several days at 100° with excess of the polysulphide. The oxidation coefficients of several such products formed at different temperatures, and carefully purified as usual, are given in Table III. Evidently they are not pure pyrite, a result somewhat surprising in view of the previous work; for if we obtain marcasite from the more acid solutions, marcasite with pyrite from those which contain less acid, and pure pyrite from practically neutral solutions, we should naturally expect pure pyrite from alkaline solutions. Further investigation has led us to believe that the products of the alkaline solutions do not contain marcasite, but are mixed with amorphous disulphide. Stokes explained, very plausibly, that the reason why marcasite gave more free sulphur than pyrite when it reacted with ferric sulphate was because it was more soluble; *a fortiori*, amorphous disulphide would give, under similar conditions, still more free sulphur because it is the most soluble of the three. The evidence for the existence of amorphous disulphide in the products of alkaline solutions is as follows: While the products of acid solutions which contain the most marcasite are the best crystallized, those from alkaline solutions which, judging by their oxidation coefficients, contain the most, are almost black, dull and lusterless at the lower temperatures. The quantity of pyrite is increased by raising the temperature or prolonging the time of reaction,—both conditions which are favorable to the crystallization of an amorphous substance. Moreover, *marcasite is not changed* by heating in alkali polysulphide solutions, as we found by heating some of the natural mineral in powdered form for several days at 300° with polysulphide of sodium. The oxidation coefficient remained 14.5. The influence of temperature on the formation of pyrite from ferrous salts and alkali polysulphides is shown in Table III. The influence of time is proved by the two following experiments: 3 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 2.5 g. Na_2S , and 0.75 g. sulphur, and 100°C water, were heated 2 days at 100° . The product contained about 75 per cent pyrite.* A similar system heated for 7 days at the same temperature gave a product containing about 95 per cent pyrite. The results are calculated on the supposition that they contain marcasite; if they contain amorphous disulphide instead, the true percentage of pyrite should of course be higher, since a given quantity of amorphous disulphide would be equivalent to a greater quantity of the less soluble marcasite, but the order of the results would of course remain the same. The products obtained at 300° were yellow,

* There is an apparent discrepancy between this last result and the one quoted in Table III under the caption " 100° ." In the latter case the excess of polysulphide was much smaller.

denser, and in direct sunlight showed a decided metallic luster, while their oxidation coefficients approach those of pure pyrite. It may therefore be safely stated that the product of the union of ferrous sulphide and sulphur from an alkali polysulphide solution is at first amorphous disulphide of iron which gradually crystallizes to pyrite.*

The formation of iron disulphide by the action of sodium thiosulphate on ferrous salts.—In the endeavor to explain the formation of pyrite and marcasite in nature, the following hypothesis presented itself. Iron disulphide of either form may oxidize under surface conditions to ferrous thiosulphate by direct addition of oxygen; this is transported by circulating waters to some point where it is reduced again to its former condition. In a partial study of the oxidation of marcasite, no trace of thiosulphate was discovered. At the same time the effort to obtain the disulphide of iron by reduction of the thiosulphate was successful. When water solutions of ferrous sulphate and sodium thiosulphate are heated in sealed tubes, even to temperatures under 100° , the iron disulphide is precipitated with sulphur. By quantitative experiments which follow, the reaction is proved to be:



Exp. 1. 5 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 18 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and 25°C water were heated in a sealed tube for 9 days at 90° . All but a trace of the iron was precipitated. The precipitate of $\text{FeS}_2 + \text{S}$ was washed in air-free water and dried in vacuo. The sulphur was extracted by carbon disulphide and the residue of FeS_2 was weighed.

	Found	Cal. from the above equation
$\text{FeS}_2 + \text{S}$	3.82	3.85
FeS_2	2.17	2.16

Exp. 2. 2 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 18 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 35°C water were sealed in CO_2 and heated for one day at about 150° . The precipitate was filtered and washed with air-free water. The solution was boiled in a current of carbon dioxide to remove a trace of hydrogen sulphide, and an aliquot part was titrated with standard iodine solution.

No. 1. $1/5$ of the solution required 16.135 g. iodine solution. Cal. for the whole, 80.675 g. iodine solution.

No. 2. $2/5$ of the solution required 32.332 g. iodine solution.

* In a recent paper (Zs. angewandte Chem., xxiv, 97, 1911), "Die Bildung von Eisen Bisulphide in Lösungen und die Entstehungen der natürlichen Pyrit-lagern," W. Feld states that whenever sulphur and ferrous sulphide are boiled in neutral or weakly acid solutions, pyrite forms.

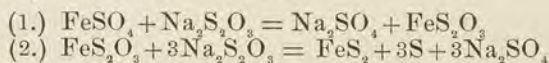
Cal. for the whole, 80.830 g. iodine solution. The iodine solution contained .005445 g. iodine per g.

80.675 and 80.830 g. iodine solution are respectively equivalent to 0.858 and 0.860 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Therefore 7.142 g. and 7.140 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were consumed in the reaction. The equation demands 7.137 g. for 5 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

	Found	Cal.
$\text{FeS}_2 + \text{S}$	1.547	1.556
FeS_2	0.872	0.863

Sodium thiosulphate when heated with water in sealed tubes forms hydrogen sulphide and sodium sulphate. $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{Na}_2\text{SO}_4$. The reaction at 200° is quite incomplete, though no thiosulphate was obtained when a solution of sodium sulphate saturated with hydrogen sulphide was heated under the same conditions. When 1 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 20°C water were heated 4 days at 200° , the thiosulphate undecomposed, as determined by standard iodine solution, was 0.753 g. 0.247 g. decomposed is equivalent to 0.141 g. Na_2SO_4 . The solution after titrating with iodine was precipitated with barium chloride. BaSO_4 found 0.223 g. equivalent to 0.136 Na_2SO_4 .

At first it was thought that the reaction between ferrous sulphate and sodium thiosulphate was to be explained as follows: (1) $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$, (2) $\text{FeSO}_4 + 4\text{H}_2\text{S} = \text{FeS}_2 + 3\text{S} + 4\text{H}_2\text{O}$. Later it was found that from *ferrous chloride* the same mixture of sulphur and FeS_2 was precipitated. Of course, the reaction represented by equation (2) could not go on with ferrous chloride. Therefore, the following is probably the true explanation of the reaction.



Form of FeS_2 obtained by heating ferrous salts with sodium thiosulphate.—Neither marcasite nor pyrite is obtained pure in this reaction. The product shows in crusts the color of pyrite, but it is poorly crystallized and may contain amorphous disulphide. A product prepared at 90° , tested by Stokes' method, behaved like a mixture of 70 per cent pyrite and 30 per cent marcasite. Another product formed at 300° * tested in the same way acted like a mixture of 72 per cent pyrite and 28 per cent marcasite. Though this reaction—the reduction of ferrous thiosulphate by sodium thiosulphate—doubtless has no significance as applied to geology, it is probable that the ferrous thiosulphate might be reduced by other reagents, and it is possible that ferrous thiosulphate may be formed in nature under some conditions, but of this we have no evidence.

* This was the maximum temperature. The reaction may have been complete before this temperature was reached.

The transformation of marcasite into pyrite.—More than fifty years ago, Wöhler* tried the experiment of heating both minerals for four hours at the temperature of boiling sulphur (about 445°) without observing any change in either of them. Our own results indicate that marcasite undoubtedly changes here, but very slowly. When marcasite was heated at 610° in hydrogen sulphide gas for 3 hours, it lost about 2.5 per cent sulphur and became strongly magnetic, owing, of course, to the formation of some pyrrhotite. A finely ground sample, after being thoroughly boiled out with hydrochloric acid, appeared decidedly yellower and less lustrous than marcasite.†

The comparison is best made by placing the sample to be tested alongside of a fragment of marcasite which has had all tarnish removed by recent boiling in hydrochloric acid (Stokes). A finely ground and purified sample of the heated marcasite gave the oxidation number 56 instead of 14 as previously. At 525° , a sample of marcasite heated $4\frac{1}{2}$ hours in hydrogen sulphide gave the oxidation number 55.8. Under similar conditions at 450° , a sample of marcasite heated 4 hours gave the oxidation number 15.7, which corresponds to 5.5 per cent of pyrite. The sample was returned to the furnace and heated again 5 hours. This time the top layer in the crucible gave, after purification, the oxidation number 27, corresponding to 53 per cent pyrite, while a deeper layer in the same crucible gave 31, which indicates about 61 per cent of pyrite. At 450° , therefore, dry heating in H_2S changes marcasite to pyrite rather slowly—50 per cent–60 per cent in 9 hours. Heated to 410° for 4 hours, the oxidation number was 13.5, showing that no measurable change had occurred.

J. Königsberger and O. Reichenheim‡ found a marked decrease in the electrical resistance of marcasite in the neighborhood of 520° . They noted that the sulphide then possessed a specific resistance of the same order as pyrite, and rightly interpreted their results to mean that marcasite had changed into pyrite and the change is irreversible. It is difficult to see in their results, however, any support of their statement that the change appears to begin between 250° and 300° , while our results contradict it.

An effort was made to effect the transformation at a lower temperature in the wet way. At 350° marcasite heated in a sealed tube with a small amount of dilute sulphuric acid partly changed to ferrous sulphate and sulphur dioxide, but the solid

* Ann. Chem. Pharm., 90, 256, 1854.

† Pyrite is naturally a more lustrous mineral than marcasite. The duller color of heated marcasite is to be ascribed to the very large number of minute crystals in the product, and the lack of continuous surfaces.

‡ Neues Jahrb., ii, 36, 1906.

portion gave no sign of change, and at 300° a powdered sample which was repeatedly heated for several days' time with sodium sulphide and polysulphide solutions was equally unaffected.

Density.—The density of the marcasite heated to 610° rose from 4.887 to 4.911. The density of pure pyrite is 5.02+. The change in color, and, more convincingly, the oxidation number, show that the substance is pure pyrite after heating, yet its density is too low. The explanation is probably to be sought in the porosity of the product.

Influence of pressure on the change marcasite \rightarrow pyrite.—Dr. A. Ludwig, at our request, kindly undertook some experiments on the influence of pressure in transforming marcasite to pyrite. A few grams of marcasite were compressed for five hours at a pressure of about 10,000 atmospheres. At the end of the period, the oxidation by Stokes' method showed no change in the substance. Later Johnston and Adams devised an apparatus in which the marcasite could be heated by a resistance coil while subjected to hydrostatic pressure of about 2000 atmospheres in petroleum oil. A number of experiments were tried between 300° and 400°, but Stokes' reaction showed no pyrite formation. The oxidation method was perhaps not quite so certain here on account of the fact that the oil was partially decomposed at the higher temperatures and the product may have contained some reducing matter which could not be removed by petroleum "ether." A mixture of pyrite and marcasite containing any such reducing impurity, as we have seen (p. 184), would give too low an oxidation number. Thus it might happen that a little pyrite could be overlooked. These experiments are of considerable interest because there are very few data on the effect of pressure in irreversible changes.* We do not know whether a difference in density in the right direction would favor the change or not, since Le Chatelier's law applies only to reversible changes. If the speed of the change is influenced by pressure quite apart from the volume relation, it may perhaps be retarded rather than accelerated. Until apparatus is developed which will give higher temperatures and at the same time high pressures, this problem must wait. At present the assumption,† which has been made in geology, that pressure favors all changes which are accompanied by reduction in volume, irrespective of their reversibility, is unwarranted.

Monotropic relation of marcasite to pyrite.—A crucible containing 50 g. pyrite was rapidly heated (20° per minute) in H_2S

* Van't Hoff, *Vorlesungen*, 2nd. Ed., Braunschweig, 1901, vol. I. p. 236.

† See Van Hise, *A Treatise on Metamorphism*, Monograph No. 47, U. S. Geol. Survey, 1904, pp. 215, 363.

over a range from 400° to 600° . The curve was perfectly smooth. When a similar charge of marcasite was heated in the same way, an acceleration of the temperature was plainly seen on the curve between 500° and 600° . (See fig. 5.) The

FIG. 5.

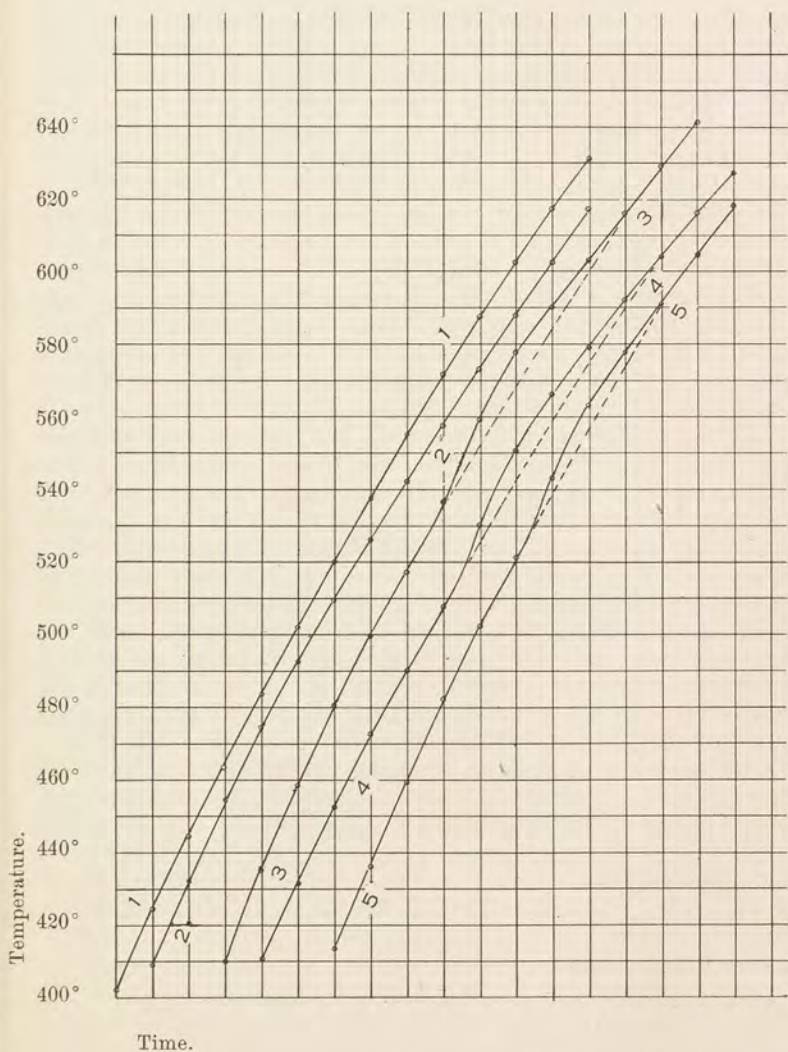


FIG. 5. Thermal curves showing evolution of heat when marcasite is changed into pyrite. (Curves 3, 4 and 5.) Curves 1 and 2 are thermal curves of pyrite.

experiment was repeated several times with similar results. Under these conditions, there is a plain evolution of heat accompanying the change of marcasite into pyrite. This shows, of course, that marcasite possesses the more energy* of the two and is a monotropic form. This condition of instability is in accord with the more rapid oxidation of marcasite in nature, and in it is probably to be found the reason for the difference in behavior between marcasite and pyrite toward other oxidizing agents. Monotropic forms often crystallize from some particular solvent or within a limited temperature range. The formation of marcasite from acid solutions is in accord with this, though as yet we do not understand the reason for it. A rise in temperature doubtless increases the velocity of the change marcasite \rightarrow pyrite. At low temperatures this becomes infinitesimal or zero; above 450° it becomes measurable. This irreversible relation has a bearing on the question of paramorphs of iron disulphide, for it is impossible to see how pyrite could change to marcasite without first passing into solution, while the opposite change is experimentally established. Paramorphs of pyrite after marcasite are certainly possible, but paramorphs of marcasite after pyrite are evidently impossible.

The agency of organic matter in the formation of natural pyrite and marcasite.—The fact that pyrite is sometimes found in nature replacing wood has been alluded to. Liversidge† gives an example of recent pyrite which is found on twigs in a hot spring at Tampo, N. Z. The sulphides of southwestern Missouri, including pyrite and marcasite, are frequently associated with asphaltic matter, and in Oklahoma this is sometimes so great in quantity as to interfere with the concentration of the ores. (Lindgren.) It is pretty generally believed by geologists that the organic matter of certain shales acted as a precipitant of the pyrite they contain. Such a shale underlies the sulphide deposits of Wisconsin. We learn from Mr. W. H. Emmons of the U. S. Geological Survey that this shale contains a small quantity of hydrogen sulphide, which naturally may have been the precipitating agent. Coals, also, in which pyrite is commonly found, are frequently permeated with hydrogen sulphide.

The role of micro-organisms in the formation of iron disulphide.—The question naturally arises whether there is any connection between organic matter and the formation of

* Cavazzi (Rend. Accad., Bologna, N. S., ii, 205, 1898) states that the heats of combustion of pyrite and marcasite are identical (1550 cal.). This is certainly incorrect.

† J. Royal Soc. N. S. Wales, xi, 262, 1877.

hydrogen sulphide. In the putrefaction of organic matter hydrogen sulphide is one of the products, and Gautier* has surmised that the pyrite which sometimes forms the substance of fossil bones and shells is precipitated by hydrogen sulphide which is given off slowly by the organic matter during its decomposition. The formation of pyrite in this case would differ from that described in the previous pages only in the source of the hydrogen sulphide, which is here a product of micro-organisms.

There is another way in which micro-organisms produce hydrogen sulphide, and that is by the reduction of sulphates. According to Beyerinck,† a considerable number of bacteria, algæ, flagellata and infusoria show this kind of activity. *Spirillum desulfuricans* is one of the most important. As these organisms are active only in neutral or alkaline solutions, ferrous sulphide is precipitated whenever ferrous salts as well as sulphates are present. The black mud of many swamps, pools, and even seas (e.g., the Black Sea), as well as sea coasts,‡ which are intermittently overflowed, contains ferrous sulphide. Mr. C. A. Davis of the U. S. Bureau of Mines, who has had large experience on this subject, informs us that he has always found hydrogen sulphide in peat-bogs into which tide-water finds its way. Apparently, the formation of pyrite or marcasite through the agency of micro-organisms has not been observed, but only an influx of air with excess of hydrogen sulphide would be needed to change the ferrous sulphide into disulphide. That micro-organisms are directly responsible for any great quantity of the pyrite or marcasite of nature seems unlikely because in the first place they are probably not active far from the surface of the ground. They have been discovered at depths of only four or five meters.§ A fraction of a per cent of free acid usually inhibits the growth of these organisms; therefore they could not live in the solutions from which marcasite appears to have formed. Pyrite and marcasite are not infrequently associated with minerals like chalcoppyrite, which proves the presence of copper in the original solutions, and copper is exceedingly poisonous to practically all micro-organisms. It is possible, however, that the reduction of sulphates like gypsum and sodium sulphate by micro-organisms may be an important source of hydrogen sulphide in nature.

Distinct conditions leading to pyrite or marcasite in nature.
—The geological relations of marcasite indicate that it is a

* C. R., cxvi, 1494, 1892.

† Centr. Bakter. u. Parasitenkunde, i, pp. 1, 49, 104, 1895.

‡ H_2S was found in sea-water by B. Leroy, Ann. Ch. Ph., lviii, 332, 1846.

§ Hygiene des Bodens, Josef von Fodor, Jena, vol. i, Pt. I, p. 137, 1893.

product of surface conditions. The oxidation of either pyrite or marcasite gives first a mixture of sulphuric acid and ferrous sulphate which by further oxidation easily gives ferric sulphate. The action of hydrogen sulphide and atmospheric oxygen simultaneously on the acid ferrous solution would lead to the same goal. We have found how hydrogen sulphide acting on acid solutions, especially in the cold, gives rise to marcasite. We have also found that above 450° marcasite could not form, thus further confirming geological deductions.

Pyrite, being a stable form, probably crystallizes under a considerably wider range of conditions than marcasite. The evidence of synthetic study is that the formation of pyrite is favored by high temperature and by solutions which contain little or no free acid. In accord with these, we have the following geological deductions. First, pyrite is a product of hot springs. In the springs of Carlsbad, which have a temperature of about 55° C., recent pyrite is observed.* The waters contain sulphates and a trace of hydrogen sulphide, and are slightly alkaline. The lagoons of Tuscany are depositing pyrite from their hot waters. Bunsen† found that the hot vapors of the fumaroles of Iceland were gradually changing the ferrous silicate of the basalts into pyrite.

More important geologically is the fact that the product of deep veins by ascending waters is always pyrite, never marcasite. Such waters are naturally hot, and commonly if not always alkaline.‡ We can now see that a separation of pyrite from a magma is entirely possible, while the temperature of any magma would doubtless be incompatible with the existence of marcasite.

The occurrence of pyrite and marcasite together.—Hintze§ mentions thirty-one instances where pyrite and marcasite are found intergrown or precipitated one upon the other. Stokes|| also tested a number of specimens which proved to be mixtures of pyrite and marcasite, some of them intergrown in concentric layers. In other places, e.g., in Joplin, Missouri, the two minerals have been observed by us in the same hand specimen.¶ According to F. L. Ransome,** the two minerals occur together, though perhaps not intergrown, in Goldfield, Nevada. These facts show very strikingly not only the small influence of nuclei in directing the form of the disulphide

* Daubrée, *Géologie expérimentale*, Paris, 1879, p. 93.

† Pogg. Ann., lxxxiii, 259, 1851.

‡ A hot acid solution in contact with carbonate or most silicate rocks would first be neutralized and then become alkaline.

§ Lehrbuch der Mineralogie, vol. i, pp. 724-778, 820-832.

|| Loc. cit.

¶ See W. S. T. Smith and Siebenthal, U. S. G. S. Folio 148.

** Private communication. Specimens were also submitted by Mr. Ransome.

which separates from solution, but also that comparatively slight differences in conditions may give rise to one or the other. Further, that the two minerals may have formed at the same time in some instances. The synthetic experiments which have been described proved that the minerals very commonly formed together,* as polymorphic forms which are monotropic are apt to do. Cold solutions which were sufficiently acid gave marcasite; warm or hot solutions, either neutral or alkaline, gave pyrite, and intermediate conditions gave mixtures.

II. Pyrrhotite.

Composition.—Special interest attaches to the composition of pyrrhotite, which, despite much discussion, is still an unsettled question. The various formulae,† Fe_xS_x , $\text{Fe}_{11}\text{S}_{12}$, $\text{Fe}_n\text{S}_{n+1}$, and FeS which have been assigned to it by various authors rest on widely varying analytical data. The analytical methods have no doubt been at fault, but the more important question concerns the physical homogeneity of the substance. This has been unusually troublesome. Pyrrhotite almost always occurs in the massive condition, a circumstance which naturally arouses suspicions of its purity, while its opacity makes it impossible to put the question to an optical test.

Many years ago Lindström‡ subjected all the known analyses of this mineral to a careful critique. Those which for any reason, such as defective analytical methods or impure material, appeared unconvincing were rejected.§ In the remainder, the ratio|| of iron to sulphur was calculated and found to vary from 1:1.06 up to 1:1.19. Some years later Habermehl¶ investigated the same question. He crushed pyrrhotite to a fine powder, covered it with water, and endeavored, by means of a strong horseshoe magnet, to separate it into fractions varying in magnetic intensity. Such fractions as he obtained in this way showed no systematic difference in composition. Habermehl used in his experiments the pyrrhotite from Bodenmais.

A very satisfactory general discussion of the question of admixtures in pyrrhotite is also given in Habermehl's paper. He decided that pyrrhotite could not contain free sulphur because carbon disulphide removes none from it, neither could

* It may be, however, that pyrite was formed first and was succeeded by marcasite as the acidity of the solution increased.

† Sidot judged from experimental work with Fe_2O_4 and H_2S that pyrrhotite should have the formula Fe_2S_4 , C. R. lxxvi, 1257, 1868.

‡ Öfv. Ak. Stockh., xxxii, No. 2, 25, 1875.

§ 13 analyses out of 43 were thus rejected.

|| In the calculation of the ratios Lindström took, in place of the small percentage of nickel found in many of these analyses, the equivalent of iron.

¶ Ber. Oberhess. Ges. für Natur- und Heilkunde, xviii, 83, Giessen, 1879.

it contain any disulphide of iron because this is insoluble in hydrochloric acid, while only sulphur remains after pyrrhotite has been boiled with this reagent. Judging from the properties ascribed to Fe_2S_3 , he concluded that this also could not be present. Habermehl was thus forced to conclude, like Lindström, though on the basis of further evidence, that pyrrhotite was variable in composition, and it may here be said that no evidence of later date has ever disproved this conclusion. At that time a homogeneous solid of variable composition was an anomaly. To-day such substances are quite generally recognized under the category of solid solutions.

Hypothesis of solid solution.—We proposed to test the hypothesis of solid solution by preparing a series of synthetic pyrrhotites and measuring some property of them. Pyrrhotite was prepared by Berzelius, Rammelsberg and others, generally by heating pyrite. One can also begin with marcasite, which, as we have seen, is first changed to pyrite between 450° and 600° , or with sulphur and iron. We have tried all three methods, though most of the work has been done with pyrite from Elba. This very pure mineral, an analysis of which was given on p. 177, Part I, was kept in a vacuum desiccator, from which portions were taken from time to time as required.

Apparatus.—The apparatus used in the synthesis of pyrrhotite appears in fig. 6. The crucible, *C*, containing the pyrite is of unglazed porcelain, 48^{mm} high $\times 37^{\text{mm}}$ outside diameter at the top and 22^{mm} at the bottom. It has a doubly perforated graphite cover, *E*, through the central orifice of which passed the glazed Marquardt jacket, *A*, which shields the thermoelement. Through the second orifice passes a similar tube, *B*, open at the lower end, which is traversed by a current of hydrogen sulphide.*

The crucible is inclosed in a large porcelain tube, *D*, $40-45^{\text{mm}}$ inside and 50^{mm} outside diameter, and 50^{cm} in length. In some of the experiments the crucible was supported in the hot zone by a strong graphite rod, *G*, which was fastened to the cover, *E*, and clamped outside the large tube, *D*, while the cover itself was fastened to the crucible by three small pegs. By means of this device, the crucible could be quickly lowered at any time to the bottom of *D* and thus rapidly cooled. In other experiments, a much shorter porcelain tube was substituted for *D*, in which instances the crucible was supported by a fire-clay pedestal which rested on the bottom of the tube. The upper

* Since the ferrous sulphide from which hydrogen sulphide is generated, contains free iron, the gas was passed through boiling sulphur to remove hydrogen, before reaching the furnace.

FIG. 6.

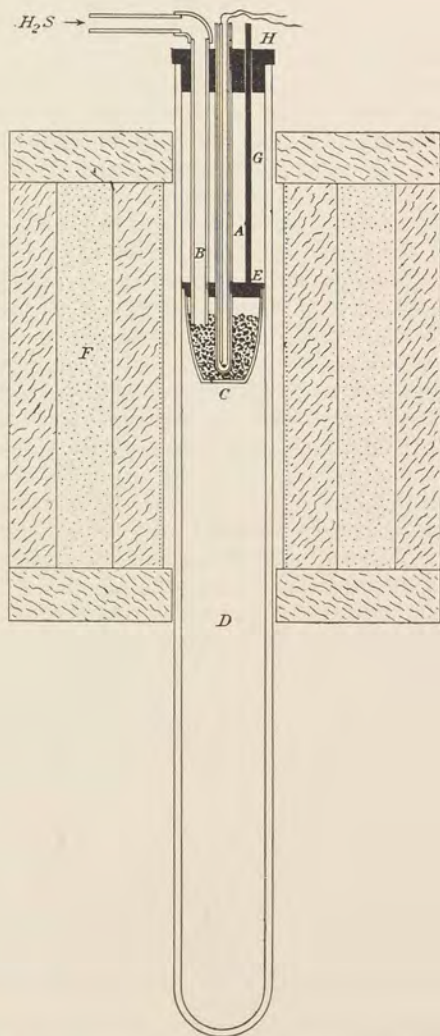


FIG. 6. Apparatus for the preparation of pyrrhotite.

end of the tube in all cases is closed by the graphite cover, *H*, through which pass *A* and *B*. The crucible and its contents are heated by a platinum-resistance furnace, *F*, as shown in the figure.

Synthesis.—When heated in hydrogen sulphide, pyrite decomposes gradually into sulphur and pyrrhotite. The decomposition may be first detected at about 575° (see p. 205). At about 665° it proceeds rapidly; still, even after some hours at 750° , the dissociation is never quite complete, and when the pyrite used is rather coarse (sized between screens of 8–40 meshes per cm.), several per cent of it persist in the product. The latter is therefore melted and cooled, and the resulting material, which is now free from pyrite,* serves as a starting point in the preparation of pure pyrrhotite.

When this is reheated it loses or gains sulphur according to conditions. A series of products was made by heating the sulphide in hydrogen sulphide for some hours at different measured temperatures, and then cooling it in nitrogen.† To facilitate the formation of homogeneous products the sulphide was carefully sized between screens of 16 and 40 meshes per cm. These products were all similar in appearance to natural pyrrhotite. They were all dense, opaque, metallic, more brownish than pyrite, and only very slightly tarnished. Some tests were made to prove that the quantity of oxide on the surface was negligible.

Weighed samples were heated in dry hydrogen to a red heat and the water formed was absorbed by passing through a calcium chloride tube. The surface of the grains became bright in a few minutes. The tube was cooled in hydrogen, which was then displaced from the apparatus by dry air. The water thus collected corresponded to less than 0.1 per cent of oxygen in two different tests. Furthermore it will be noted later that the preparations which were cooled in nitrogen were comparable in density with those which were prepared in another way and were not tarnished in the slightest degree (see p. 199).

Composition of synthetic pyrrhotite.—The sulphur was determined in each of the synthetic pyrrhotites by a method‡ worked out in this laboratory, which was proved accurate within at least 0.2 per cent of the sulphur present.

Treitschke and Tannmann§ state that the fused sulphide of

* Except for a slight superficial layer which decomposes in the next process.

† The nitrogen was prepared by Knorre's method (Die Chem. Ind., xxv., 531, 550, 1902; Chem. Centralb., i, 125, 1903), i. e., by dropping a saturated solution of sodium nitrite from a dropping funnel into a solution of ammonium sulphate and potassium chromate. The gas was passed through dilute sulphuric acid to remove ammonia, and then successively through long columns of chromic acid to remove oxides of nitrogen; sulphuric acid to remove moisture, and finally over-heated copper to remove oxygen, or any traces of oxide of nitrogen which may have escaped.

‡ Allen and Johnston, Jour. Ind. & Eng. Chem., ii, 196, 1910; Zs. anorg. Chem., lxi, 102, 1911.

§ Z. anorg. Chem., xlix, 320, 1906.

iron corrodes and dissolves porcelain, but it should be noted that they made their fusions in carbon-resistance furnaces without further protection from the air.

Our unglazed crucibles appeared quite unattacked in an atmosphere of hydrogen sulphide. Analyses revealed the presence of about 0.25 per cent of silica in our preparations, though we believe that most of this was derived from minute fragments of the crucible, which are difficult to exclude entirely when the cake of sulphide is broken out of the crucible. Thus No. 7 gave 0.33 per cent, No. 10, 0.26 per cent, and No. 3 gave 0.22 per cent and 0.24 per cent of silica in duplicate determinations. This of course includes the silica in the original pyrite, which, however, was negligible, —.04 per cent.

Relation of the specific volume to the composition.—The specific gravity* of each preparation was determined and from

TABLE IV.†

Composition, density and specific volumes of pyrrhotites.

	Total Sulphur	Cal. FeS	Cal. dissolved S.	Sp. gr. at 25°	Cal. dens. at 4°	Cal. Sp. V.
1	36.72	99.59	.41	4.769	4.755	0.2103
2	36.86	99.37	.63	4.768	4.755	0.2103
3	37.71	98.04	1.96	4.691	4.677	0.2138
4	38.45	96.89	3.11	4.657	4.643	0.2154
5	38.54	96.73	3.27	4.646	4.632	0.2159
6	38.64	96.57	3.43	4.648	4.634	0.2158
7	38.84	96.26	3.74	4.633	4.619	0.2165
8	39.09	95.86	4.14	4.602	4.589	0.2179
9	39.49	95.23	4.77	4.598	4.585	0.2181
10	40.30	93.96	6.04	4.533	4.520	0.2212

† *Conditions of formation.*

1. From pyrite, melted in H_2S , kept a little above m. p. for 1 h. in nitrogen and then cooled in nitrogen.
2. From sulphur and iron, otherwise like 1.
3. From pyrite, heated to equilibrium in H_2S at 1300° , then quickly cooled.
4. From pyrite, heated in H_2S to 900° , then cooled in nitrogen.
5. From pyrite, melted in H_2S and cooled rather slowly in same.
6. From marcasite, melted in H_2S and cooled rather slowly in the same.
7. From pyrite, heated to 800° 6 h. in H_2S , then cooled in nitrogen.
8. From pyrite, heated to 700° $2\frac{1}{2}$ h. in H_2S , then cooled in nitrogen.
9. From pyrite, heated to 600° 3 h. in H_2S , then cooled in nitrogen.
10. From pyrite, heated to 600° 15 h. in H_2S , then quickly cooled in the same.

* Day and Allen, Publication No. 31, p. 55, Carnegie Institution of Washington.

this the density (at 4°) and the specific volume was calculated. Table IV contains these data. Column 1 contains the total percentage of sulphur, Columns 2 and 3 the quantities of FeS and S calculated on the hypothesis that pyrrhotite is a solid solution of sulphur in ferrous sulphide. In fig. 7 are plotted as abscissas the quantities of dissolved sulphur (Column

FIG. 7.

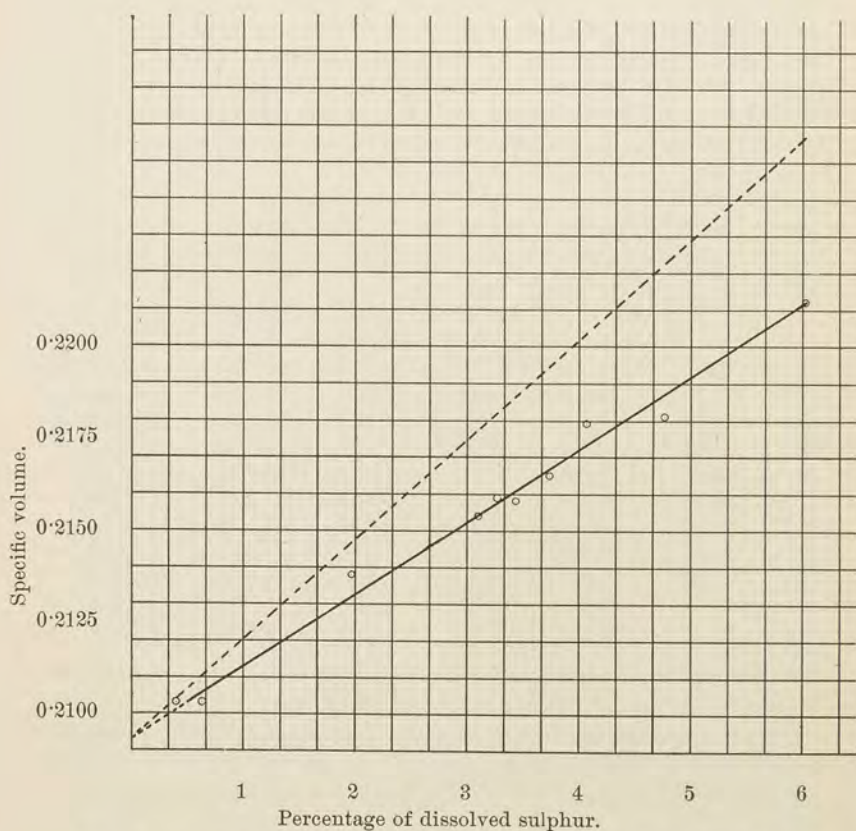


FIG. 7. The variation of specific volume with the dissolved sulphur in pyrrhotite.

3, Table IV), and as ordinates the specific volumes (Column 6, Table IV). It will be noticed that the scale of the plot is very large and the locus of the points is not only a continuous curve as the theory of solid solutions demands, but it is also a straight

line within the limits of the errors.* If we compare this line with the dotted line joining the specific volumes of sulphur and ferrous sulphide, we see that a considerable contraction has taken place in the process of solution.†

Equilibrium between solid pyrrhotite and the partial pressure of sulphur in hydrogen sulphide.—The composition of a variable phase of two components, iron and sulphur, as pyrrhotite is shown to be, would of course be fixed when both temperature and pressure are fixed. By heating in hydrogen sulphide the pressure is fixed, though not independently of the temperature. To obtain equilibrium, the products were heated for about three hours, at the measured temperature, and then by the device shown in fig. 6, the crucible and its contents were quickly lowered to the bottom of the enclosing tube. The process of heating and quick cooling in hydrogen sulphide was repeated until the density of the product was constant. The densities of the products thus successively prepared usually agreed exactly in the third decimal place. The rate at which the sulphur is absorbed by pyrrhotite in the cooling is too slow to affect these results except possibly in the determinations made at the highest temperatures (1100° – 1300°), where a small quantity of sulphur may perhaps be taken up. As this point is important, some data on the rate at which the cooling proceeded are here given.

Initial temperature	1300°	1100°	800°	600°
Temperature after 1 min.	-----	680°	-----	-----
“ “ 2 “	-----	580°	480°	-----	-----
“ “ 3 “	-----	-----	-----	420°	-----
“ “ $3\frac{1}{2}$ “	-----	-----	400°	-----	-----
“ “ 5 “	-----	-----	-----	-----	305°
“ “ 6 “	-----	365°	-----	-----	-----
“ “ 10 “	-----	-----	165°	-----	-----

In Table V are collected the quantities of sulphur dissolved in pyrrhotite at different temperatures in hydrogen sulphide gas. The sulphur in Nos. 1 and 6 was determined by analysis; in the rest it was calculated from the specific gravity. The results in Table VI, showing the dependence of composition on temperature when the products are cooled in nitrogen, are given by way of control. In fig. 8, the curve in space shows how the composition of pyrrhotite varies with both tempera-

* Three of the points are beyond the errors of the determination of sulphur, and specific gravity, but if we allow a small error in homogeneity in the process of preparation, probably occasioned by the splinters of porcelain, the statement holds for these points also.

† The density of rhombic sulphur is very nearly 2.075, and its specific volume is therefore 0.4819. The specific volume of the ferrous sulphide is estimated by extrapolation to be 0.2093.

ture and pressure. The discontinuity in the curve between 1165° and 1200° which is conditioned by the change of state will be discussed later (p. 207).

Maximum percentage of sulphur in pyrrhotite.—The most concentrated solution of sulphur in ferrous sulphide obtained

FIG. 8.

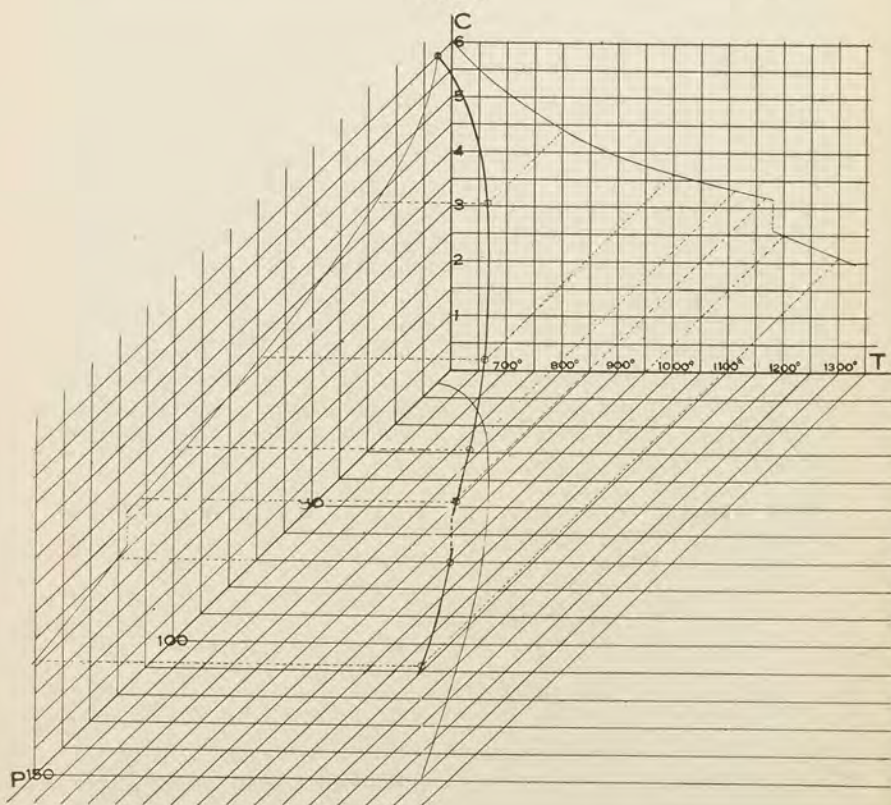


FIG. 8. Curve in space showing the dependence of the composition of pyrrhotite on temperature and pressure.

C (composition) = percentage of dissolved sulphur.

P = pressure in millimeters of mercury.

T = temperature.

synthetically contains 6 per cent of sulphur and 94 per cent of FeS. This solution was obtained at 600° , where the absorption of sulphur from hydrogen sulphide is slow. At 575° the reaction was so slow that the attempt to get a saturated product was discontinued. At 550° , as we will show farther on, pyrite is formed. The curve in fig. 9 shows an extrapola-

TABLE V.

Sulphur dissolved by FeS in an atmosphere of H₂S
at measured temperatures.

	Temperature	Time of heating		Percentage of dissolved sulphur
		Time in which equilibrium was reached	Total	
1	600°	12 h.	15 h.	6.04
2	800°	3 "	7 "	4.41
3	1000°	2 "	4 "	3.6
4	1100°	2 "	4 "	3.3
5	1165°	1 "	2 "	3.2
6	1200°	20 min.	1½ "	2.5
7	1300°	20 "	1 "	1.96

TABLE VI.

Sulphur in pyrrhotite cooled in nitrogen from
various temperatures.

	Temperature	Time of heating in H ₂ S	Percentage of dissolved sulphur
1	1210°	Few minutes	.41
2	About 1200°	1½ h.	.63
3	1000°	6 h.	2.70*
4	900°	6 h.	3.11
5	800°	6 h.	3.74
6	700°	2½ h.	4.14
7	600°	3 h.	4.77

*The sulphur in No. 3 was calculated from the density.

tion from which we judge the maximum quantity of sulphur in pyrrhotite obtained by heating in hydrogen sulphide must be about 6.5 per cent. If we compute the analyses of natural pyrrhotite in terms of FeS and S, we find that the limit of solubility agrees well with this. The highest value calculated from Lindstrom's† figures is 6.08 per cent. From Rose's‡ analyses we derive the value of 6.76 per cent. The maximum percentage of sulphur in the pyrrhotite analyses quoted by Dana§ is 40.46 per cent. This particular occurrence, however, contained about 0.5 per cent of copper and cannot, therefore, be satisfactorily

† Loc. cit.

‡ Gmelin Kraut Handbuch der Ch., 6th Ed., Vol. III, pt. 1, 332.

§ System of Mineralogy, 6th Ed., p. 74.

used for a calculation of this sort. Dana gives also an analysis of pyrrhotite by Funaro, which contained 40.27 per cent total sulphur, equivalent to 6 per cent of dissolved sulphur. This pyrrhotite contained also 3.16 per cent of nickel, which, according to Penfield, is mechanically intermixed with pyrrhotite in the form of pentlandite. If this be true, the ratio of sulphur to

FIG. 9.

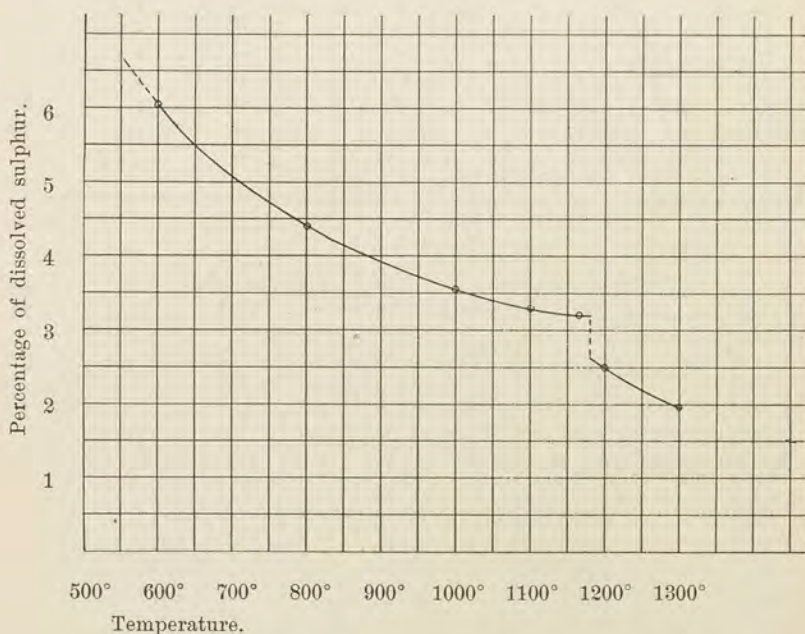


FIG. 9. Curve showing the percentage of sulphur dissolved by ferrous sulphide in hydrogen sulphide gas as the temperature varies.

iron in the pyrrhotite would be raised a little, since pentlandite belongs to the type of sulphides MS , and the equivalent quantities of iron and nickel are almost the same.

Some allowance for errors in the analyses of the natural mineral should be made; still, the agreement between the maximum quantities of sulphur in the natural and synthetic pyrrhotite is striking.

Relation between pyrrhotite and pyrite.—The diagram in fig. 10 shows the relation between pyrrhotite and pyrite. The curve 1, 1 shows the partial pressures of sulphur vapor in one atmosphere of hydrogen sulphide, as they vary with temperature. These results are taken from Preunner and Schupp,* and

* Zs. phys. Chem., lxxviii, 161, 1909.

are extrapolated above 1130° and below 750° . Curve 2, 2, represents so far as may be with partial data the dissociation pressures of pyrite at various temperatures. Here it is assumed that the vapor pressure at 665° is one atmosphere (see p. 205). At 550° pyrrhotite was found to pass over into pyrite when

FIG. 10.

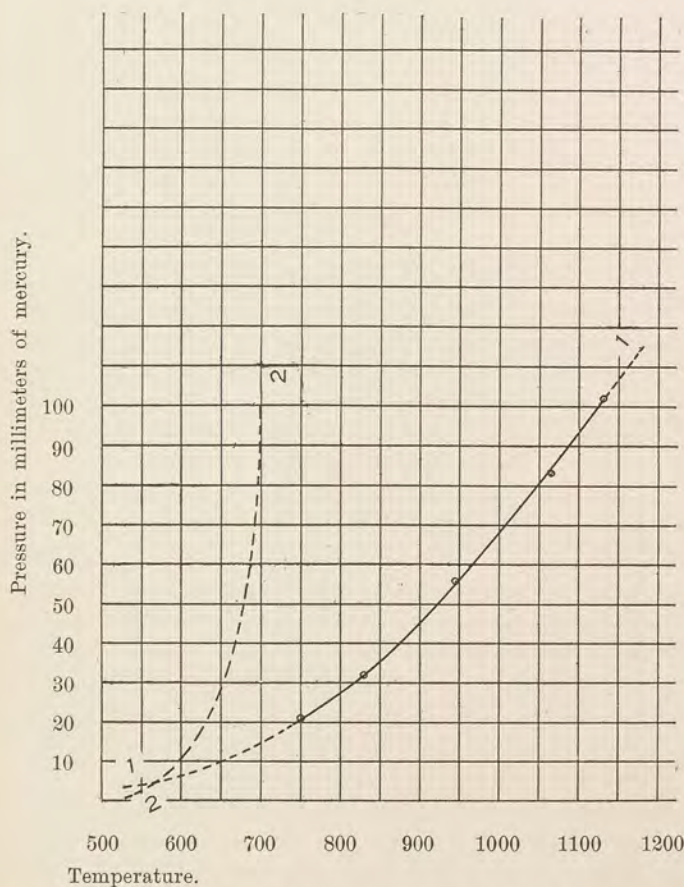


FIG. 10. Curve 1, 1, shows the partial pressures of sulphur in hydrogen sulphide at various temperatures (Preunner and Schupp). Curve 2, 2, shows approximately the dissociation pressure of pyrite.

heated in hydrogen sulphide. This was proved by the fact that the color changed to the yellower color of pyrite and the density increased, whereas pyrrhotite decreases in density with increase of sulphur. At 575° pyrrhotite showed no change in

FIG. 11.

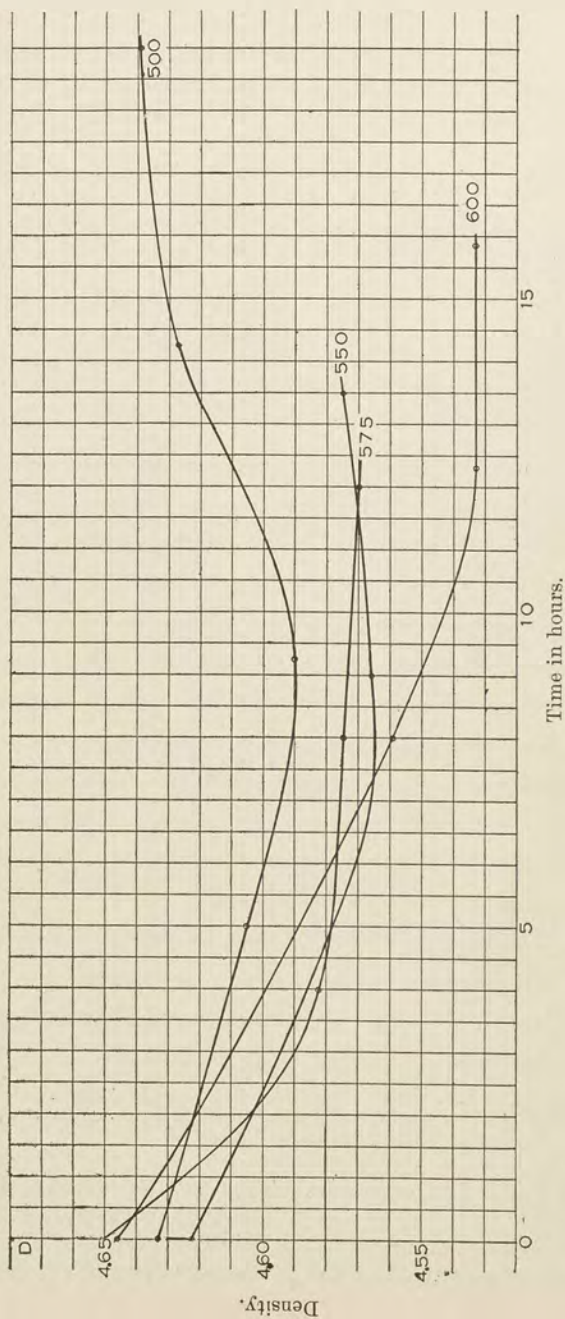


FIG. 11. Curves showing the change in specific gravity with time on heating pyrrhotite in hydrogen sulphide. The curves refer to the temperatures 500°, 550°, 575° and 600°.

color but continued to decrease in weight the longer it was heated. These facts are graphically shown in fig. 11. Pyrite under the same conditions gave inside of a few hours a perceptible quantity of pyrrhotite, which was proved by testing with warm hydrochloric acid. At 565° the pyrite formed in several hours only a doubtful trace of pyrrhotite, if any. Between 550° and 575° , therefore, the two curves 1, 1 and 2, 2 cross, and, at that point, about 565° , at a pressure of about 5^{mm} of sulphur, pyrite should be in equilibrium with a pyrrhotite containing about 6.5 per cent of dissolved sulphur. How this quantity would vary with conditions we do not yet know, though, as we have just seen, the solution of sulphur in ferrous sulphide of maximum concentration found in nature, formed presumably from water solutions, does not vary much from it.

The change from pyrite to pyrrhotite is, then, a reversible reaction, $\text{FeS}_2 \rightleftharpoons \text{FeS}(\text{S})_x + (1-x)\text{S}$. Since the system contains a gaseous phase, the temperature at which the change occurs is manifestly dependent on pressure.

Dissociation point.—It has been previously stated that pyrite undergoes dissociation into pyrrhotite and sulphur and that this dissociation is detectable at 575° after the lapse of several hours, when the heating is done in hydrogen sulphide. If the heating is continued at a moderate rate (2° per min.) a strong absorption of heat manifests itself at about 665° . Here, under these conditions of heating, the dissociation therefore becomes suddenly accelerated, and it is probable that the pressure of the escaping sulphur reaches one atmosphere. The solid phases pyrite and pyrrhotite, i. e., the saturated solution of sulphur in ferrous sulphide, should at a fixed temperature maintain a fixed pressure. As a matter of fact, the point is not sharp; the temperature gradually rises through an interval of about 20° . This is probably due to the formation of a coating of pyrrhotite on the pyrite grains, which retards the dissociation, so that the system requires a gradually rising temperature to maintain the pressure. The fact that undecomposed pyrite persists so tenaciously in the product seems to support this view. A typical thermal curve for pyrite in this region is shown in fig. 12. It is seen to have the same general form as a melting point curve and the end of the heat absorption is more sharply marked than the beginning, though for the reasons stated the latter has the greater significance. The following data show that the absorption ends pretty uniformly at about 685° :

El. V	6050 mv. = 686°
"	6037 mv. = 684°
El. S	6083 mv. = 686°
"	6060 mv. = 684°

Inversion in ferrous sulphide.—Le Chatelier and Ziegler* discovered a transformation in commercial ferrous sulphide at about 130° . This has been confirmed by Treitschke and Tammann† and by Rinne and Boeke.‡ The last named

FIG. 12.

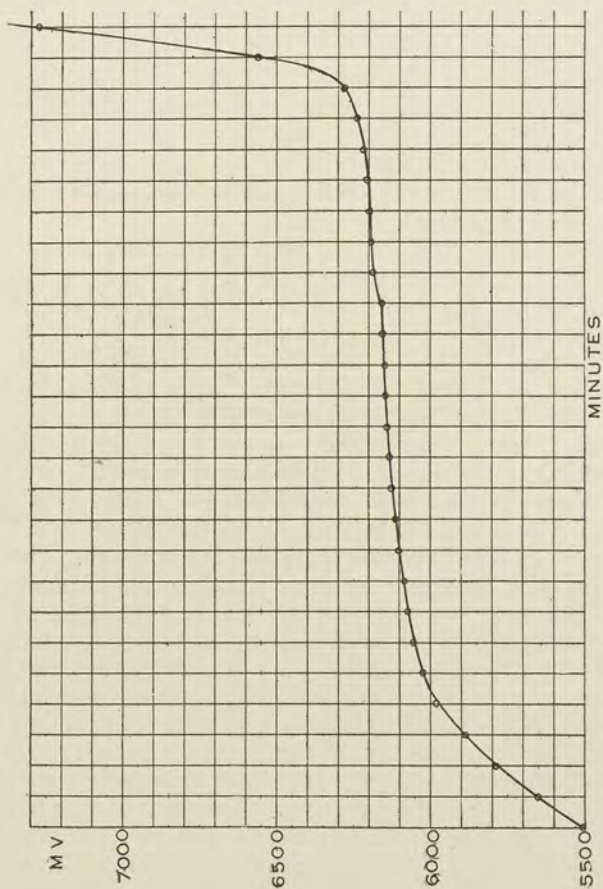


Fig. 12. Curve showing the dissociation of pyrite into pyrrhotite and sulphur.

authors were unable to find any heat absorption in approximately pure ferrous sulphide, though the addition of iron (or carbon), which they believe goes into solid solution, makes the heat change manifest. The dissolved iron is supposed by

* Bull. Soc. d'Encouragement de l'Industrie, Sept. 1902, 368.

† Loc. cit.

‡ Zs. anorg. Chem., liii, 338, 1907.

Rinne and Boeke to facilitate the transformation, first by raising the temperature at which it takes place, and second by loosening the crystal structure. The transformation point in the presence of 7 per cent dissolved iron is found to be 138° , and further addition of iron does not change it. At lower temperatures a temperature interval is found, and the inversion is lowered, but the temperature cannot be followed in mixtures containing less than 5 per cent dissolved iron. Our results confirm the above in so far as the experiments were carried. The change could not be detected in pyrrhotite or pure troilite. It is a natural inference that the change *does take place in these also*, but that presumably the heat absorption in them is very gradual and is therefore overlooked.

Melting temperature of pyrrhotite.—Pyrrhotite melts in hydrogen sulphide at 1183° . (Table VII.) Of course, a solid solution melts through an interval and not at a point, but we have as yet no quantitative methods which enable us to determine the length of such an interval at high temperatures. The maximum of the heat absorption falls at the above point. The melts seem to be quite thin,* and there is usually little or no undercooling, if the temperature is not too rapidly lowered.

TABLE VII.

Preparation	Thermoelement	Melting temperatures		Freezing temperatures	
		mv.	degrees	mv.	degrees
1	V	11589	1181	11590	1181
2	"	11585	1181		
3	"			11585	1181
4	A	11683	1183		
5	"	11687	1183		
6	"	11675	1182		
6	"	11700	1184		
7	"	11705	1184		
8				11690	1183

Examples of freezing and cooling curves of pyrrhotite in hydrogen sulphide are plotted in fig. 13. By reference to fig. 9 we notice that the liquid pyrrhotite contains still a considerable excess of sulphur above the ferrous sulphide ratio, and that the quantity is less than it is in the solid. From Beckmann's formula† for the change of melting temperature with

* See Friedrich, *Metallurgie*, vii, 257, 1910.

† Ostwald's *Lehrbuch der Chemie*, vol. ii, pt. 3, p. 38.

composition in a solid solution $\Delta = \frac{0.02 T^2}{l} (C_1 - C_2)$, where Δ is the change in the melting point, T is the melting point (absolute) of the solvent, l is the heat of fusion of the same, and C_1 and C_2 the concentrations of the solute in the liquid and solid respectively, we find that the melting temperature is raised if

FIG. 13.

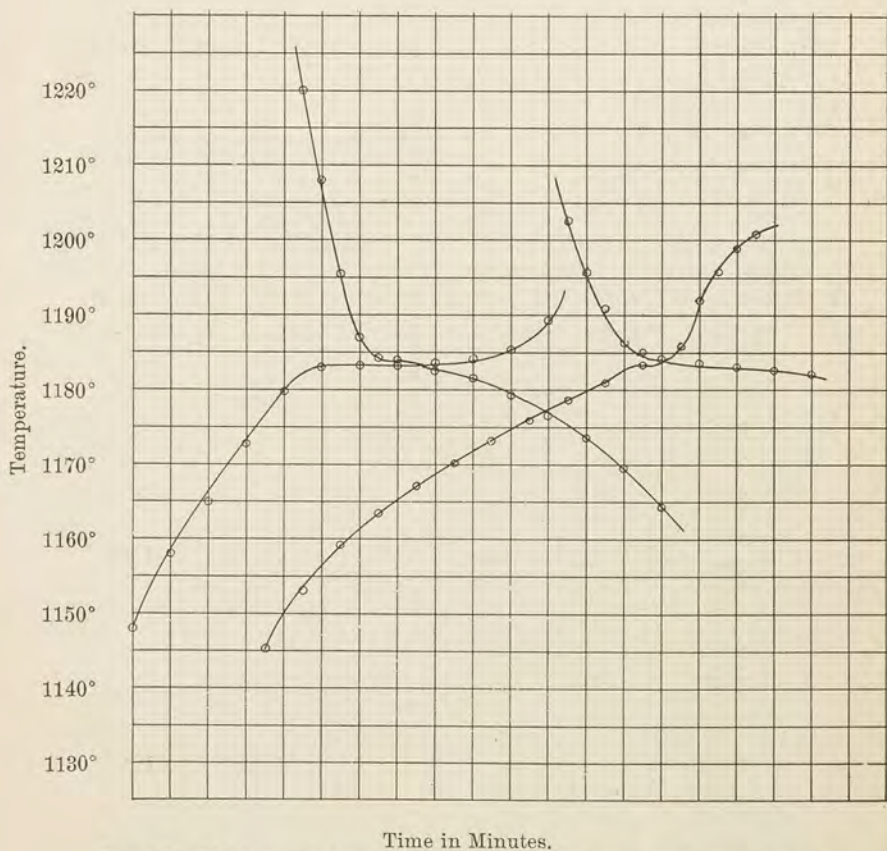


FIG. 13. Melting and freezing curves of pyrrhotite in hydrogen sulphide.

the *liquid which first forms* contains less of the solute than the original solution. We do not, to be sure, know the composition of the *first* liquid which forms, but as the *final* liquid product contains less sulphur than the original solid, it is impossible to believe that this is not the case with the first liquid also.

Melting temperature of pyrrhotite in sulphur vapor.—If this conclusion is correct, it follows that by raising the pressure

of the sulphur vapor in which the pyrrhotite is melted, the quantity of sulphur in the product should also be raised, and the melting point with it. In accord with expectation, the maximum heat absorption in melting was raised about 5° when the change of state took place in an atmosphere of sulphur vapor. The apparatus used was the same as that shown in fig. 6, except that a second furnace below the one shown in the figure was used for boiling the sulphur. At the bottom of the tube were placed 100 grams of sulphur, and the temperature of the lower furnace (measured outside the tube) was raised gradually to a little above the boiling point of the sulphur, and only after the sulphur burned freely at the top of the tube was the temperature of the crucible raised through the melting interval. The experimental data follow:

El. A -----	11740 m. v.	1188°
	11726 "	1187°
	11720 "	1186°

The maximum heat absorption is only about 5° higher than it is when the pyrrhotite melts in hydrogen sulphide. A careful comparison with the latter on a succeeding day in the same apparatus left no doubt as to the reality of rise in the temperature and as to its order of magnitude.

Melting temp. of pyrrhotite in H_2S on the
succeeding day, with the same element
and otherwise same conditions -----

11683 m. v.	1183°
11686 m. v.	1183°

Melting point of ferrous sulphide, FeS .—Since the melting temperature of pyrrhotite is raised by increasing the pressure of sulphur vapor above it, pure ferrous sulphide must melt at a temperature lower than any of the sulphur solutions. In the effort to obtain this point the crucible containing the pyrrhotite was heated in a vacuum furnace. The dissolved sulphur volatilized in vacuo, as expected, but there was a further loss, though a slow one, which was found to be due to a dissociation of the ferrous sulphide into the elements, a circumstance which naturally prevented the exact location of the melting point.

The apparatus employed is shown in fig. 14. *A* is a glazed porcelain tube, closed at one end, 50^{cm} in length. The open end is closed by the perforated brass plug *D*, through which passes the porcelain tube *B* which protects the thermoelement *E* from the action of the fused sulphide. This plug has a side tube also of brass which connects with the pump. An airtight joint between the tube and plug is made with Kotinski cement, *CC*. It was found necessary also to close the tube *B* by

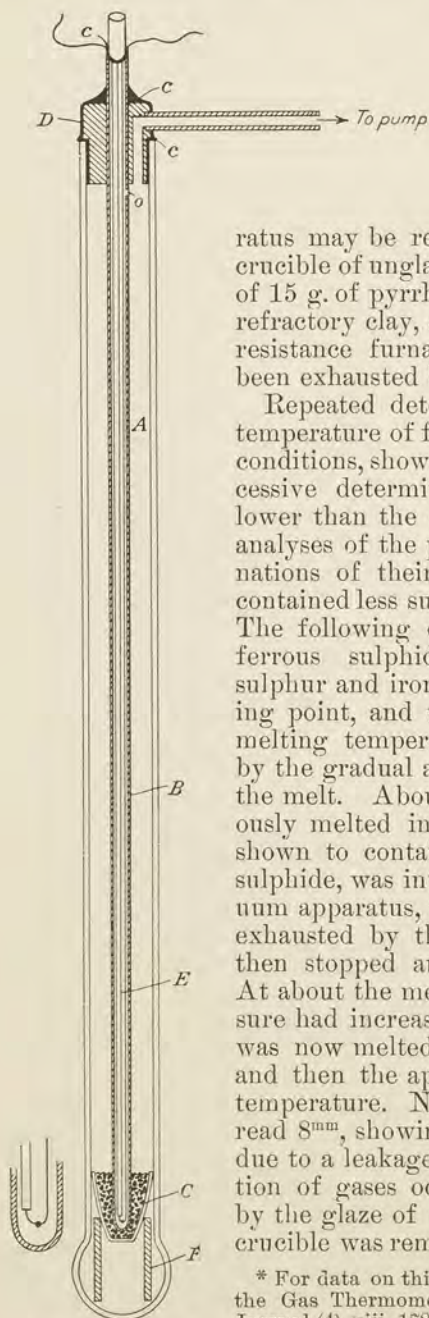


FIG. 14. Vacuum furnace.

cementing in a small glass plug, because the former invariably leaked through the closed end. A small hole is drilled through this tube at *O*, so that all the air in the appa-

ratus may be removed by the pump. The crucible of unglazed porcelain has a capacity of 15 g. of pyrrhotite. It rests on a ring of refractory clay, and is heated as usual by a resistance furnace after the apparatus has been exhausted by the oil pump.

Repeated determinations of the melting temperature of ferrous sulphide under these conditions, showed in general that each successive determination was a few degrees lower than the one which preceded it, and analyses of the products as well as determinations of their density showed that they contained less sulphur than ferrous sulphide. The following data make it evident that ferrous sulphide slowly dissociates into sulphur and iron, in the vicinity of its melting point, and that the successively lower melting temperatures obtained are caused by the gradual accumulation of free iron in the melt. About 15 g. of a sulphide previously melted in the vacuum furnace, and shown to contain less sulphur than ferrous sulphide, was introduced again into the vacuum apparatus, which was then completely exhausted by the pump. The pump was then stopped and the heating was begun. At about the melting temperature the pressure had increased to 9.5^{mm} . The product was now melted and frozen several times, and then the apparatus was cooled to room temperature. Next morning the manometer read 8^{mm} , showing that the pressure was not due to a leakage but doubtless to the evolution of gases occluded by the crucible and by the glaze of the porcelain.* When the crucible was removed from the vacuum tube

* For data on this point, see Holborn and Day, *On the Gas Thermometer at High Temperatures*, this Journal (4), viii, 178, 185, 1899; Guichard, *The Gases Disengaged from the Walls of Tubes of Glass, Porcelain, and Silica*, C. R., clii, 876, 1911.

the contents were found to possess a bright metallic luster, while about 10^{cm} above the cover of the resistance furnace a ring of sulphur was condensed on the inside of the tube. This experiment was repeated with similar results. A sulphide containing 36.02 per cent of sulphur (FeS contains 36.45 per cent) was heated as before. This time the manometer read 5.5^{mm} at the melting temperature. When the apparatus was cold the reading was 5.0^{mm} . This product was also perfectly bright and a ring of sulphur was again visible* on the cool part of the tube. The product was analyzed again and found to have lost still more sulphur. The following table (Table VIII) shows that the percentage of sulphur, the specific gravity, and the last melting point of three different products prepared in vacuo are in accord, i. e., the density increases with the percentage of free iron and the melting "point" falls. The melting temperature of No. 3 should of course be lower than No. 2, but these temperatures are not easy to locate exactly; a part of the difficulty is perhaps due to the fact that we are dealing with a mixture, in which the heat absorption is not sharp.

TABLE VIII.
Properties of pyrrhotite after melting in vacuo.

No.	Melting temperature in microvolts	Melting temperature in degrees	Sp. gr. at 25°	Density (4°)	Sp. vol.	Per cent sulphur	Free iron calculated
1	11508	1165	4.816	4.802	.2082	36.02	1.23%
2	11346	1156	4.861	4.847	.2063	35.71	2.08
3	11416	1157	4.883	4.869	.2054	35.41	2.91

It is quite evident from the above data that the true melting point of ferrous sulphide can only be determined by heating in sulphur vapor, the pressure of which is equal to the dissociation pressure of the sulphide. We may safely say that this point will be found to lie between 1183° , the melting temperature of a product formed in hydrogen sulphide of one atmosphere pressure, and 1165° , and that the point is within 5° of 1170° . Treitschke and Tammann,† working with impure material, by extrapolation estimated the melting point of ferrous sulphide at 1300° . Biltz,‡ heating precipitated sulphide of

* The sulphur was identified by solution and crystallization from carbon bisulphide. About 100% was thus recovered.

† Zs. anorg. Chem., xlix, 328, 1906.

‡ Zs. anorg. Chem., lix, 273, 1908.

iron in an atmosphere of nitrogen, obtained $1197^{\circ} \pm 2^{\circ}$. Friedrich, who took considerable pains with the composition of his material, preparing it by the fusion of synthetic pyrrhotite with the calculated quantity of iron, found an average of 1171° .*

Crystals of pyrrhotite.—Measurable crystals of pyrrhotite were readily formed by the action of hydrogen sulphide on solutions of ferrous salts in glass tubes which contained some air. The yield was small and it cannot be stated, in the absence of optical tests, that the different crystals were identical in composition; in fact, Mr. Larsen finds crystallographic evidence that there were differences of composition. The manifest impossibility of finding the composition of individual crystals and of proving that the crystals of any one preparation were identical, made it useless to attack the interesting question, how the angles in crystals of the pyrrhotite series vary with composition. Crystals were prepared at 80° , at 225° , and at some other temperatures, therefore presumably above and below the inversion temperatures, but in the absence of direct evidence on either pure ferrous sulphide, or pyrrhotite of any composition (see p. 206) this can not be stated with certainty. Mr. Larsen believes there is good crystallographic evidence for two crystal forms, the upper form orthorhombic, the lower hexagonal.

Troilite and its relation to pyrrhotite.—The knowledge of troilite is defective on account of the scarcity and poor development of material, but the analyses on record, and its behavior towards acids, prove that it is essentially ferrous sulphide, contaminated generally with the sulphides of cobalt and nickel. The mineral is found only in meteorites embedded in a matrix of metallic iron, and it is evidently the contact with free iron and not the peculiar conditions of meteorite formation which accounts for the lack of dissolved sulphur in troilite. It is probable that the stony portions of meteorites contain ordinary pyrrhotite.†

Lorenz‡ has described a method for the preparation of ferrous sulphide (artificial troilite) which depends on the same principle, i. e., formation in the presence of excess of iron. Metallic iron is simply heated to redness in hydrogen sulphide. Crystalline crusts of silvery luster which are easily detached from the unchanged metal, are produced in this way. Analyses of these crusts by Lorenz approached ferrous sulphide, but not closely. The only determination of sulphur gave 37 per cent, which corresponds to 0.85 per cent of dissolved sulphur. Two products were made by us in this way. They agreed with Lor-

* Loc. cit.

† Dana, A System of Min., 6th Ed., p. 73.

‡ Ber., xxiv, 1501, 1891.

enz's description completely, but they were not ferrous sulphide. The first, formed at 850° from soft iron wire, had a specific gravity at 25° of 4.739, corresponding to a specific volume (4°) of 0.2116. The second, formed at 950° , had a sp. gr. of 4.748, corresponding to a specific volume of 0.2112. Making no allowance for the impurities in the iron, we calculate from these numbers (see p. 198) 1.1 per cent and 0.9 per cent of dissolved sulphur respectively. The diffusion of sulphur into the iron is evidently too slow here to give a homogeneous product. An examination of these crystals under the microscope, for which the authors are indebted to Dr. F. E. Wright, showed that they were either hexagonal or pseudohexagonal, but they were not adapted to measurement on the goniometer.

Efforts to prepare ferrous sulphide in the wet way were no more successful. Weinschenk* claims to have formed it by the action of hydrogen sulphide on a solution of ferrous chloride in sealed tubes. The product consisted of microscopic hexagonal plates, which Weinschenk states did not lose sulphur when heated to redness in hydrogen and therefore were ferrous sulphide. His experimental work is doubtless in error, for Habermehl,† many years earlier, had shown that pyrrhotite under these conditions loses sulphur continuously and gradually approaches pure iron.

Weinschenk's work was repeated by us. Pure ferrous chloride was prepared repeatedly with much care, dissolved in an aqueous solution of carbon dioxide and subjected to the action of hydrogen sulphide, made in several ways (by the action of the water on sodium thiosulphate; and by the action of dilute sulphuric acid on ammonium thiocyanate). In no case was pure ferrous sulphide obtained. Free sulphur, either from secondary reactions or perhaps from the dissociation of hydrogen sulphide, even at 200° , always appeared to give pyrrhotite. After our further experience in heating pyrrhotite in vacuo, we state with confidence that pure ferrous sulphide has doubtless never been made.

Mineralogically, troilite has no claim to a separate mineral species any more than have pyrrhotites of different composition; it is simply the end member of the series of solid solutions. This is abundantly attested by the synthetic evidence submitted in the foregoing pages. It may also be noted by way of further evidence that the specific gravity of natural troilite or rather the specific volume calculated from it, agrees tolerably well with the extrapolated value in fig. 7, and the best crystallographic‡ work on troilite, imperfect though the material was, indicates that it is hexagonal, as it should be.

* Zs. Kryst., xvii, 499, 1890.

† Loc. cit.

‡ Linck, Ber., xxxii, 895, 1899.

Application of data on pyrrhotite to geology.—Very little of the chemistry of pyrrhotite worked out in these pages will probably find application in geology. However, the following points have a practical bearing.

1. The readiness with which pyrrhotite changes to pyrite, and the reverse, has been specially noted. The transformation of pyrrhotite into pyrite through the agency of vein-forming solutions which probably contained polysulphides, is an observed fact in geology; but the dissociation of pyrite has apparently not been noted, although certain phenomena in the vicinity of contacts would suggest this. The most distinct phenomenon which points to such a reaction is the almost constant presence of pyrrhotite in contact metamorphic shales. In such shales pyrite develops normally at some distance from the contact, while close to it, pyrrhotite is universally present and there is little, if any, pyrite. (Lindgren.) The occurrence of pyrrhotite which could be proved to have formed in this way would point to a temperature above 500° ,—much higher if the dissociation occurred under considerable pressure. Pseudomorphs of pyrite after pyrrhotite do not seem to have been observed, but they would probably be readily formed by the action of polysulphides on pyrrhotite crystals. Pseudomorphs of marcasite after pyrrhotite have been described by Schöndox and Schroeder* and by Pogue.† The synthetic experiments (see p. 179) suggest that these were formed by the addition of sulphur from slightly acid solutions containing hydrogen sulphide and free sulphur in suspension.

2. The possibility of the formation of pyrrhotite from slightly acid solutions at temperatures as low as 80° has been made clear in the foregoing pages. The crystals made in this way were generally associated with crystals of pyrite and perhaps marcasite, a fact which shows how readily the former unite with sulphur. This is probably the reason why the pyrrhotite of nature never seems to form under the above conditions, for such could only occur in surface solutions where there is more or less access of air. This, with hydrogen sulphide, would give free sulphur.

3. Pyrrhotite is regarded in certain instances as a primary constituent of eruptives. Its intimate intergrowth in such cases with silicates such as augite and olivine strongly suggests the conclusion that both have separated from a common magma. Now it is well known that molten sulphides of this sort are all but immiscible with molten silicates; in other words, a system like this would separate into two layers. It would be a matter of great interest to determine whether the addition of water, aqueous sodium sulphide or even of a more complex solution

* Jahrest. Niedersächsischen geol. Vereins Hannover, p. 132, 1909.

† Proc. U. S. Nat. Mus., xxxix, 576, 1911.

would bring a two-layered system of this character to homogeneity, but at present the problem is experimentally beyond our means.

III. Crystallographic Study.

As the sulphides of iron are all opaque, the ordinary optical tests are not available and the mineralogic study is confined to the determination of the color, luster, cleavage, magnetic properties, crystal form, chemical properties, etc. Color and magnetism are important diagnostic properties of the sulphides of iron, while the crystal form and the chemical properties give positive evidence of the identity of the artificial preparations with the natural minerals. In general the synthetic iron sulphides prepared in the dry way or by the inversion of one form into another in the solid state are massive and without crystal form, and only the color, magnetic and chemical properties can be determined. The iron sulphides precipitated from solutions usually consist of a network of crystals, or of drusy crusts. Some preparations have crystals which are large enough for measurement on the Goldschmidt goniometer; most of the crystals measured are from 0.2 to 0.4^{mm} in length, though one crystal of β -pyrrhotite is about a millimeter in length, and one crystal of marcasite is even a little larger. In many of the preparations the crystals are all very minute—less than a tenth of a millimeter in length and often much less—and the crystallographic study was confined to an examination of the material under the microscope. The crystal habit, however, of each of the four minerals is characteristic, and even the minute crystals can usually be determined.

Pyrite.

In some preparations the larger crystals of pyrite are half a millimeter across and can be easily recognized with a pocket lens by their color and crystal form. Much smaller crystals can be determined by the use of the microscope. The crystals usually show both the cube and the octahedral faces, but both forms also occur alone; pyritohedrons were not observed; the faces are always much warped and very imperfect. For the several crystals measured on the goniometer, the angles were seldom over half a degree from the theoretical value, and a closer agreement cannot be expected.

Marcasite.

The color of the synthetic marcasite is identical with that of the natural mineral, but the color test is not altogether satisfactory on minute crystals, even when brightened by heating in acid. The crystal habit, however, is characteristic, and the goniometric measurements of some of the larger crystals show a very close agreement with those of the natural mineral.

The common habit of the synthetic marcasite is shown in clinographic projection in fig. 15. The crystals are twinned with the face m $\{110\}$ * as twinning plane, they are tabular parallel to the twinning plane and elongated along the vertical axis. The prisms m $\{110\}$, especially the large faces parallel to the twinning plane, are deeply striated parallel to the base. The domes e $\{101\}$ and l $\{011\}$ are also prominent. Crystals of a second habit, which are common in some preparations, are more symmetrical in their development and less often twinned; in them the domes, e $\{101\}$ and l $\{011\}$, are characteristic forms

FIG. 15.



FIG. 16.

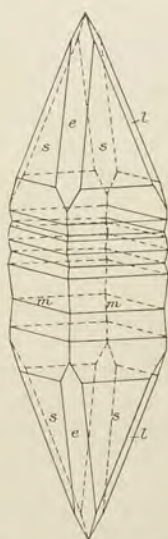


FIG. 15. Artificial marcasite showing the forms m $\{110\}$, e $\{101\}$, and l $\{011\}$. Twinned after $\{110\}$.

FIG. 16. Artificial marcasite showing the forms m $\{110\}$, e $\{101\}$, l $\{011\}$, and s $\{111\}$.

and the striated prisms, m $\{110\}$, are usually prominent. The crystal represented in fig. 16 is of this habit, but the prisms and pyramids s $\{111\}$ are more prominent than usual. Several crystals were seen under the microscope which resemble the fiveling pictured by Dana.† A preparation formed as usual, but at room temperature, consists of strings of minute crystals which have a rhombic outline under the microscope, and sometimes the obtuse angle of the rhombs is truncated by a face which is probably the prism, m $\{110\}$.

*Throughout this paper parentheses are used to indicate crystal faces; brackets, to indicate the entire crystal form.

† System of Mineralogy, 6th edition, p. 95.

Crystals of marcasite large enough for measurement on the goniometer were found in several preparations; most of them are only a few tenths of a millimeter in length, but a few are about a millimeter long. Seven fairly satisfactory crystals from two different preparations were measured. Only one of these is not twinned. The signals were seldom sharp, blurred signals, striated zones, and vicinal faces being the rule. The faces of $\{111\}$ usually gave fairly sharp reflections, but between (111) and $(11\bar{1})$ there was a more or less complete band of signals, and that for the face (110) seldom stood out sharply from the others. In some of the tabular twinned crystals the faces of $\{110\}$ which are parallel to the twinning plane yielded bright signals, or else there were several bright signals near these faces. The reflections from the faces of $\{011\}$ were usually bright, but vicinal development often made their exact position uncertain. Between (011) and $(01\bar{1})$ there was usually a dim series of signals, but the reflection signals of the faces of $\{011\}$ did not stand out from the others. The faces of $\{101\}$ gave fairly sharp signals. In one crystal the reflections of the faces of $\{772\}$ took the place of those from $\{111\}$ at the ends of the series of signals of this zone. Most of the twinned, tabular crystals gave a dim but nearly continuous line of signals from the large faces (110) through the face (011) and the corresponding face $(01\bar{1})$ to $(\bar{1}\bar{1}0)$. The faces $\{10\bar{1}\}$ of both individuals lie on this zone, whose symbol is $h+l=k$. It is poorly developed on the untwinned crystal.

Crystal angles of synthetic marcasite.—Of the seven crystals to be described, the first five were from a preparation of October 16, 1908, and were formed by the action of H_2S on an acid solution of $FeSO_4$ for four days at a maximum temperature of 300° . The crystals of this preparation are all of the habit shown in fig. 15. Crystals 6 and 7 were from a preparation of October 28, 1908, and were formed at a maximum temperature of 220° . The common habit of the crystals of this preparation is shown in fig. 16, but the pyramids and prisms are often less prominent; there are some twinned crystals similar to those shown in fig. 15.

Table IX lists the weighted average of the angles measured for each crystal, the crystal constants of synthetic marcasite, and the corresponding constants of the natural mineral as given by Gemacher and Goldschmidt.

The agreement shown by Table I between the angles and axial ratios of natural marcasite and those of the synthetic mineral is very good. Both commonly show twinning with (110) as twinning plane, and both have the two unit domes and the pyramids as common faces. The base, however, which is

TABLE IX.
Crystal angles measured on synthetic marcasite.

No. of Crystal	No. of meas.	Polar angle of (011)	No. of meas.	Polar angle of (111)	No. of meas.	Polar angle of (101)	No. of meas.	(110) (010)	No. of meas.	Angle between twin of after meas. (110)	No. of meas.	Polar angle of (772)
1	1	50° 58'		----		----	2	52° 41'	3	74° 42'	3	----
2	2	50° 40'		----		58° ±	2	52° 12'	1	74° 33'	1	81° 50'
3	3	50° 44'		----		----	6	52° 36'	2	74° 20'	6	81° 48'
4	6	50° 18'		----		----	6	52° 35'	1	75° 12'		----
5	5	49° 55'	8	63° 40'		57° 27'	5	52° 34'	1	74° 47'		----
6	2	49° 55'	6	63° 29'		58° 10'	5	52° 38'	3	----		----
7	4	50° 40'	6	63° 22'		57° 50'	4	52° 28'	2	75° 18'		----
Weighted av.		50° 27'		63° 29'		57° 48'		52° 35'		74° 49'		81° 48'
Computed		50° 36'		63° 29'		57° 52'		52° 35½'		74° 49'		81° 53½'
Gemacher*		50° 36'		63° 30' 54"		57° 55' 59"		52° 41'		----		----
Goldschmidt† ...		50° 29'		63° 30'		57° 59'		52° 50'		----		----

$a : b : c = 0.7646 : 1 : 1.2176$ Larsen, synthetic marcasite

$a : b : c = 0.762256 : 1 : 1.21698$ Gemacher*

$a : b : c = 0.7580 : 1 : 1.2122$ Goldschmidt†

$a : b : c = 0.75241 : 1 : 1.18473$ Hausmann

$a : b : c = 0.766172 : 1 : 1.23416$ Sadebeck

* Natural marcasite, Gemacher, Zs. Kryst., xiii, 242, 1888.

† Natural marcasite, Goldschmidt, Winkeltabellen, Berlin, 1897.

usually prominent in the natural mineral, was not observed on the synthetic crystals, while the prism zone is often more prominent on the artificial crystals. The natural mineral is described as having the brachydomes and pinacoids deeply striated parallel to the edge (010) (001); the synthetic mineral is similarly striated, the pyramid and prism zones are even more prominently striated parallel to the base, and the zone $h + l = k$ on some of the crystals is a more or less continuous series of faces due to striations.

Pyrrhotite.

The experiments of Rinne and Bøeke* show an inversion in FeS with 7 per cent, the maximum amount, of dissolved iron at 138°. On decreasing the amount of dissolved iron to 5 per cent the absorption of heat takes place between 90° and 98°. Although they were not able to observe a heat absorption in FeS with less than 5 per cent of dissolved iron or in natural pyrrhotite, they state that the inversion takes place but is too sluggish to be observed. Ferrous sulphide with a little carbon showed the inversion at 134.5°, while meteoric troilite with a little carbon inverted at about 143°.

The present crystallographic study tends strongly to confirm the work of Rinne and Bøeke. The low temperature form or β -pyrrhotite appears to be hexagonal, while the high temperature form or α -pyrrhotite appears to be orthorhombic. The measured interfacial angles for the two forms are near together and the fact that these angles vary with the amount of sulphur in excess of that required for FeS, together with the impossibility of determining the chemical composition of the measured crystals, makes a comparison of the crystal constants of the two forms impossible. However, the crystal habit, the twinning, and the development of the faces on the two forms afford good evidence for the view that they belong to different crystal systems.

The color of the synthetic pyrrhotite is similar to that of the natural mineral. That prepared by melting iron and sulphur together is a little darker and has more of a grayish cast than the natural mineral. The crystals from some preparations of α -pyrrhotite are only slightly magnetic while those from others are strongly so. The crystals always show polarity with the poles along the a -axis. The poles for β -pyrrhotite are along the c -axis in the one crystal observed.

α -Pyrrhotite.

Twenty-two fairly satisfactory crystals of α -pyrrhotite, representing four different preparations, were measured on the

* Zs. anorg. Chemie, liii, 338-343, 1907.

goniometer. The crystals are almost certainly orthorhombic in symmetry, although the angles in the prism zone are very nearly 60° . In the following discussion, the crystals are treated as orthorhombic. The crystals are usually twinned

FIG. 17.

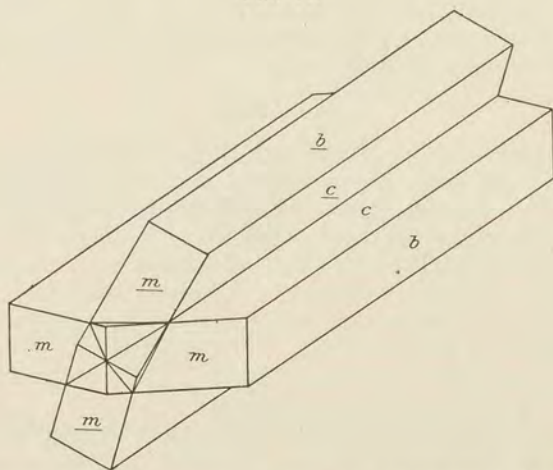


FIG. 17. Artificial α -pyrrhotite showing the forms $m \{110\}$, $b \{010\}$, and $c \{001\}$. Twinned after (023) .

FIG. 18.

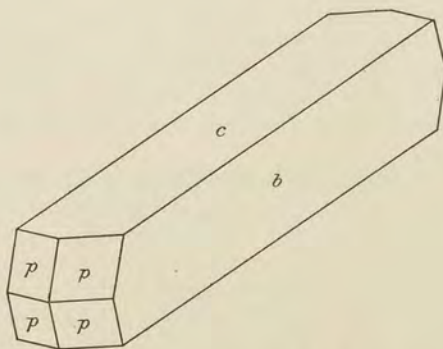


FIG. 18. Artificial α -pyrrhotite showing the forms $b \{010\}$, $c \{001\}$, and $p \{111\}$.

with the twinning plane (023) ; one crystal is twinned only after (021) , and two crystals are twinned after both laws. The twinned crystals are tabular parallel to the base and elon-

gated in the direction of the a -axis. The untwinned crystals are also nearly always much elongated along the a -axis, and have as their principal forms $\{001\}$, $\{010\}$, $\{111\}$. Tabular crystals of hexagonal shape are rare.

Crystals A to H are from two different preparations formed by the action of H_2S on an acid solution of $FeSO_4$ at a maximum temperature of $225^\circ C$. They are about $0.3 \times 0.15 \times 0.05$ mm in dimensions. Most of the crystals are tabular parallel to the base and elongated along the a axis; they are twinned after (023) ; $\{001\}$, $\{010\}$, and $\{110\}$ are

FIG. 19.

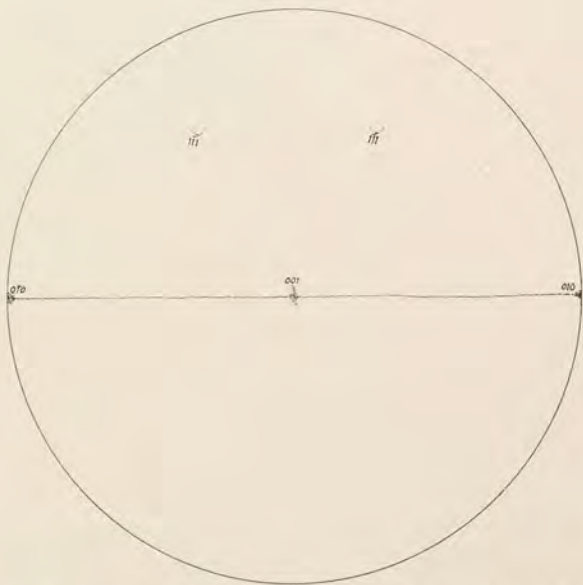


FIG. 19. Stereographic projection of a simple crystal of α -pyrrhotite showing the development of the striation and vicinal faces.

the dominant forms. Fig. 17 shows one of these crystals. Crystal H simulates a tabular hexagonal crystal; it is not twinned and is bounded by the forms $\{001\}$, $\{010\}$, $\{110\}$, $\{011\}$, $\{112\}$, $\{021\}$, and $\{111\}$. Crystals of this type are uncommon.

A third preparation was formed at about $200^\circ C$. The inside tube contained 3 g. $FeCl_2$, 1 cc 20 per cent HCl , and 25 cc boiled H_2O . After heating at about $200^\circ C$. for several days, the sealed tube was allowed to stand at room temperature from June 16, 1909 to March 23, 1910. There was a considerable

yield of pyrrhotite crystals. They are strongly magnetic and show polarity with the poles along the a axis. Many of them are about 0.3mm in length and about a fifth as thick and broad. Twinning is rare and the base resembles a hexagon much elongated along one diameter and delicately striated parallel to the six sides. There are a very few hexagonal tablets and twinned crystals similar to those of preparations 1 and 2. The six measured crystals, I to N, are all similar in habit to the crystal

FIG. 20.

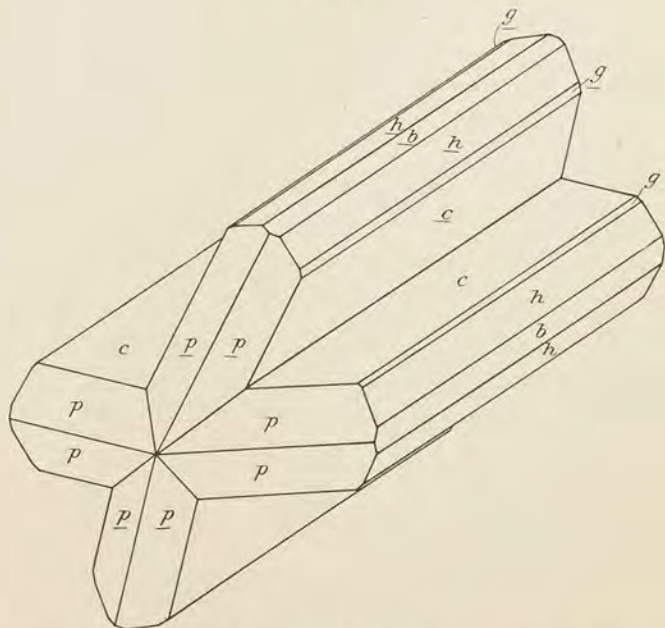


FIG. 20. Artificial α -pyrrhotite showing the forms c {001}, b {010}, p {111}, h {021}, and g {011}. Twinned after {021}.

shown in fig. 18, and the dominant forms are {001}, {010}, and {111}. One crystal showed also the form {021} poorly developed, and another crystal showed {091}. Fig. 19 is the stereographic projection of crystal I. The crystals were mounted along the a axis. They did not, in general, give sharp signals and measured angles between (001) and (010) were in some cases out as much as 2° ; while the measurements for the faces {111} were only a little better.

A fourth preparation was formed by the action of H_2S on a solution of acid FeCl at a maximum temperature of 210° . Nearly all of the crystals are tabular parallel to the base and

elongated along the a axis. Several of them are 0.5mm in length. Out of seven crystals measured, one is twinned after the law: twinning plane (021); three are twinned after the law: twinning plane (023); two after both laws, and one crystal is an untwinned hexagonal tablet. The crystals resemble the untwinned crystals of lot 3 in that the dominant forms are $\{001\}$, $\{010\}$, and $\{111\}$, but $\{021\}$, $\{011\}$, $\{0.1.20\}$, $\{110\}$, and $\{112\}$ were also recognized. Fig. 20 represents one of these crystals twinned after (121). Fig. 21 is the stereographic projection of crystal U, which is twinned after both (023) and (021). One of the individuals of the twin after (023) is poorly developed on the part of the crystal shown.

FIG. 21.

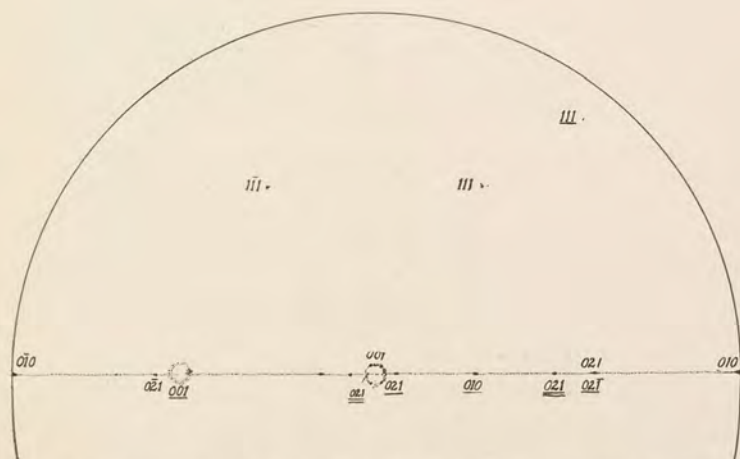


FIG. 21. Stereographic projection of a crystal of α -pyrrhotite twinned after both (021) and (023). The half of the crystal represented on the projection shows few of the faces of one of the individuals after (023). The faces of the crystal twin after (021) are underscored once, those of the twin after (023) twice.

Table X gives a summary of all the crystals of α -pyrrhotite which were measured. The designation of the crystal is given in column one and the number of the preparation from which it came in column two. Column three lists the faces recognized on the crystal, and column four gives the average of the angle between the faces (110) and (010). The eight succeeding columns give the weighted averages of the measured interfacial angles each followed by the value of p_o computed from that angle. Next to the last column lists the weighted averages of the constant p_o which is equal to the vertical axis, c . The final column gives all measured angles not listed in any of the previous columns.

TABLE X.—SUMMARY OF CRYSTAL

Crystal	No. of Preparation	Faces represented	(010) (110)	Angle betw. basal pinacoids of twin after (023)	p_o	Angle betw. basal pinacoids of twin after (021)	p_o	(001) (021)
A	1	(001) (010) (110) (112)	$60^\circ \pm$	$66^\circ 30'$	0.9834	-----	-----	-----
B	1	(001) (010) (110)	$59^\circ 32'$	$65^\circ 35'$	0.9850	-----	-----	-----
C	1	(001) (010) (110)	$59^\circ 50'$	$65^\circ 7'$	0.9578	-----	-----	-----
D	2	(001) (010) (110) (100) (011) (023)	$60^\circ 10'$	$65^\circ 27'$	0.9639	-----	-----	-----
E	2	(001) (010) (110)	$59^\circ 57'$	$63^\circ 59'$	0.9376	-----	-----	-----
F	2	(001) (010) (111) (221)	$60^\circ \pm$	$64^\circ 5'$	0.9388	-----	-----	-----
G	2	(001) (010) (110) (992)	$59^\circ 57'$	$65^\circ 57'$	0.9732	-----	-----	-----
H	2	(001) (010) (110) (021) (111) (011) (112)	$60^\circ \pm$	-----	-----	-----	-----	$62^\circ 44'$
I	3	(001) (010) (111)	$60^\circ 22' \pm$	-----	-----	-----	-----	-----
J	3	(001) (010) (111) (091)	$59^\circ 56'$	-----	-----	-----	-----	-----
K	3	(001) (010) (111)	$60^\circ 5'$	-----	-----	-----	-----	-----
L	3	(001) (010) (111)	$59^\circ 36'$	-----	-----	-----	-----	-----
M	3	(001) (010) (111)	$60^\circ 4'$	-----	-----	-----	-----	-----
N	3	(001) (010) (021) (111)	$59^\circ 59'$	-----	-----	-----	-----	$63^\circ 15'$
O	4	(001) (010) (021) (111) (011) (112)	$59^\circ 53'$	$65^\circ 30'$	0.9648	-----	-----	$62^\circ 31'$
P	4	(001) (010) (021) (111)	$60^\circ \pm$	-----	-----	-----	-----	$62^\circ 14'$
Q	4	(001) (010) (021) (111) (071)	$60^\circ \pm$	-----	-----	$55^\circ 18'$	0.9545	$62^\circ 19'$
R	4	(001) (010) (110) (021) (111) (0.1.20)	$60^\circ \pm$	$65^\circ \pm$	-----	-----	-----	$62^\circ 26'$
S	4	(001) (010) (110) (021) (111) (011)	$59^\circ 44'$	$66^\circ 10'$	0.9772	-----	-----	$62^\circ 18'$
T	4	(001) (010) (021) (111) (011)	$60^\circ \pm$	$62^\circ 50'$	0.9160	$52^\circ 25' \pm$	-----	$61^\circ 38'$
U	4	(001) (010) (021) (111) (011) (1.1.34)	$60^\circ 30' \pm$	$64^\circ 40'$	0.9495	$55^\circ 30'$	0.9503	$62^\circ 8'$

A comparison of the different values of p_o with the average value, c , for any crystal shows that the difference is greater than 2 per cent only for crystal A, and in this case the angle from which p_o was computed was so unreliable that it was not considered in computing the average. In all cases where the angle from which any p_o was computed seemed to be reliable the difference between p_o and c is less than 1 per cent of c . An error as large as 1 per cent in c may, therefore, be regarded

MEASUREMENTS OF α -PYRRHOTITE

p_o	(111)	p_o	(011)	p_o	(112)	p_o	Average $p_o = c.$	Other measured angles
	(001)		(001)		(001)			
-----	-----	-----	-----	-----	43° 50'	0.9610	0.9834	-----
-----	-----	-----	-----	-----	-----	-----	0.9850	-----
-----	-----	-----	-----	-----	-----	-----	0.9578	-----
-----	-----	-----	44° 10'	0.9713	-----	-----	0.9639	(001) (021) = 32° 27'
-----	-----	-----	-----	-----	-----	-----	0.9376	-----
-----	61° 48'	0.9372	-----	-----	-----	-----	0.9380	(001) (221) = 74° 59'
-----	-----	-----	-----	-----	-----	-----	0.9732	(001) (992) = 83° 41'
0.9701	62° 44'	0.9750	43° 59'	0.9646	43° 59'	0.9675	0.9725	-----
-----	63° 24'	1.0035	-----	-----	-----	-----	1.0035 ±	-----
-----	63° 1'	0.9878	-----	-----	-----	-----	0.9878	(001) (091) = 83° 17'
-----	62° 55'	0.9827	-----	-----	-----	-----	0.9827	-----
-----	62° 32'	0.9667	-----	-----	-----	-----	0.9667	-----
-----	63° 9'	0.9927	-----	-----	-----	-----	0.9927	-----
0.9920	63° 4'	0.9891	-----	-----	-----	-----	0.9891	-----
0.9614	62° 34'	0.9681	43° 51'	0.9607	44° 12'	0.9772	0.9669	-----
0.9497	62° 14'	0.9545	-----	-----	-----	-----	0.9521	-----
0.9530	-----	-----	-----	-----	-----	-----	0.9530	(001) (071) = 81° 40'
0.9578	-----	-----	-----	-----	-----	-----	0.9578	(001) (0.1.20) = 2° 42'
0.9524	62° 40'	0.9772	43° 50'	0.9601	-----	-----	0.9660	-----
0.9262	61° 58'	0.9437	43° 10'	0.9380	-----	-----	0.9267	-----
0.9456	62° 10'	0.9517	-----	-----	-----	-----	0.9485	(001) (1.1.34) = 3° 10'

as exceptional. One possible exception is crystal I, as the measurements on it were unsatisfactory and it has, therefore, been discarded in the discussion to follow. If, however, we compare the value of c for the different crystals we find a maximum difference of 0.0660 between crystals M and T or a difference of nearly 7 per cent of their mean value. Moreover, the two extremes are neither exceptionally high nor exceptionally low but the other crystals are pretty evenly distributed

between them. It seems certain, therefore, that the crystal constants of *a*-pyrrhotite vary considerably in accord with the variable composition of the mineral.

A further study of Table X shows that while the crystals of a given preparation show a considerable difference in the constant, *c*, yet those of preparation 3 are uniformly high, those of preparation 4 generally low, and those of preparation 1 and 2 intermediate. Unfortunately it was not found possible to determine the relation between the value of *c* and the chemical composition, as, even were any of the crystals large enough for an analysis, it is probable that they are built up of successive shells of different composition.

No consistent variation in the angle (100) (110) was recognized but it probably varies with *c*. The measurements were usually not good but the average value of $59^{\circ} 55'$ is probably within $15'$ of the true value. Computing the axial ratios of *a*-pyrrhotite for the limiting values given by crystals M and T we have: $a:b:c$ 0.5793:1:0.9267 to 0.5793:1:0.9927. It is probable that the limits are considerably greater than this. Table XI lists the observed faces and the interfacial angles as computed from the above values of the axial ratios.

The symmetry and crystal constants of a-pyrrhotite.—The evidence that *a*-pyrrhotite is orthorhombic in symmetry is good, although it may not be conclusive. The angles in the prism zone were not proven to differ from sixty degrees, but the habit of the crystals consistently indicates orthorhombic rather than hexagonal symmetry. A very few crystals resembled hexagonal tablets. Nearly all of the crystals of the first two preparations were developed much like the crystal shown in fig. 17, although small domes and pyramids were found on many of the measured crystals. The habit and the development of different faces in the zone (*o k l*) from those in the zone (*h h l*) strongly indicate orthorhombic symmetry. The crystals of the third preparation were, with few exceptions, developed as is the crystal shown in fig. 18. The development of the zonal and vicinal faces is shown in fig. 19, which is a stereographic projection of crystal I. The other crystals of this lot are much like this, although the striations of the zone (*o k l*) are not usually so prominent. The crystals of the fourth preparation are usually twinned, and the common habit of these crystals is shown in fig. 20. This crystal is twinned after (021) and the crystals which are twinned after (023) are similar, except for the twinning law. These crystals are also elongated along the *a* axis and show a very different development in the zone (*o k l*) from that in the zone (*h h l*). Fig. 21, which is a stereographic projection of crystal U, shows the development of the zonal and vicinal faces. Several other

TABLE XI.—Computed interfacial angles of α -pyrrhotite for different values of the axial ratios.

	$c = 0.9267$	$c = 0.9927$
(001) (011)	$42^{\circ} 49'$	$44^{\circ} 47'$
(112)	$42^{\circ} 42'$	$44^{\circ} 40'$
(021)	$61^{\circ} 39'$	$63^{\circ} 16'$
(111)	$61^{\circ} 36'$	$63^{\circ} 13'$
(010)	$90^{\circ} 0'$	$90^{\circ} 0'$
(110)	$90^{\circ} 0'$	$90^{\circ} 0'$
(100)	$90^{\circ} 0'$	$90^{\circ} 0'$
(023)	$31^{\circ} 42'$	$33^{\circ} 30'$
(221)	$74^{\circ} 52'$	$75^{\circ} 50'$
(010) (110)	$59^{\circ} 55'$	$59^{\circ} 55'$
(100) (100)	$90^{\circ} 0'$	$90^{\circ} 0'$
Angle between twins after (023)	$63^{\circ} 24'$	$67^{\circ} 0'$
Angle between twins after (021)	$56^{\circ} 42'$	$53^{\circ} 28'$

preparations were made up largely of crystals of high-temperature pyrrhotite, and, although no measurable crystals were found, the microscopic study showed that they were very similar in habit to the measured crystals. On the other hand, the crystals from the three preparations which were formed at 100° C. and below, invariably had a very different habit (p. 228).

β -Pyrrhotite.

Three crystals of pyrrhotite formed below the inversion temperature were measured. They were each from a different preparation and should give a fair idea of the crystal habit and crystal constants of β -pyrrhotite. Their habit and the measured angles afford good reasons for supposing that β -pyrrhotite is hexagonal. The most prominent faces recognized were those of $m\{10\bar{1}0\}$ and $z\{20\bar{2}1\}$, but those of $c\{0001\}$ were rather prominent on one crystal, and the vicinal form $z_a\{16.0.\bar{1}6.7\}$ on two crystals; the faces of the form $x\{50\bar{5}1\}$ were subordinate on one crystal. All three of the crystals were twinned with $(10\bar{1}1)$ as the twinning plane, giving cruciform twins with an angle of approximately 90° between the two individuals. Figures 22 and 23 are clinographic projections of the two habits of the crystals.

The best crystal came from a preparation which was formed by heating for 8 days at a maximum temperature of 80° C. a

sealed glass tube which contained a dilute solution of FeSO_4 saturated with H_2S at 0°C . The yield of β -pyrrhotite was small and consisted of the measured crystal which was about 1^{mm} in length, a crystal about half as large and a few crystals less than 0.2^{mm} in length. All were twinned and otherwise

FIG. 22.

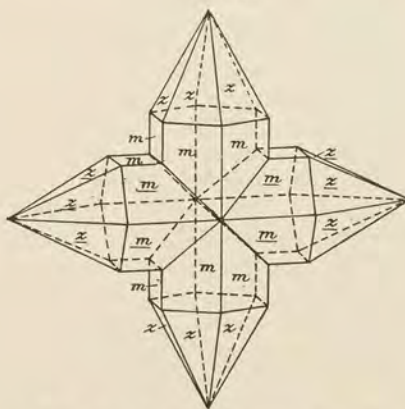


FIG. 23.

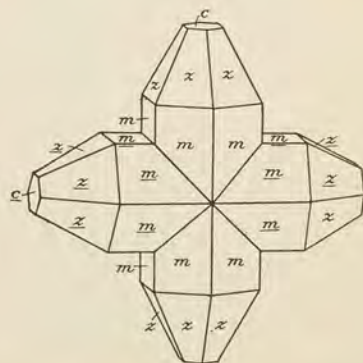


FIG. 22. Artificial β -pyrrhotite showing the forms $m\{10\bar{1}0\}$ and $z\{20\bar{2}1\}$. Twinned after $(10\bar{1}1)$.

FIG. 23. Artificial β -pyrrhotite showing the forms $m\{10\bar{1}0\}$, $z\{20\bar{2}1\}$, and $c\{0001\}$. Twinned after $(10\bar{1}1)$.

similar to the measured crystal. This crystal, which was mounted on the goniometer along the c -axis of one of the individuals, gave blurred and multiple signals, but it was not striated, and most of the faces could be located to within about ten minutes. The only forms developed were the prisms $\{10\bar{1}0\}$ and the steep pyramids $\{20\bar{2}1\}$. Figure 22 is the clinographic projection of the crystal. Six fairly good measurements of the angle $(20\bar{2}1) \wedge (20\bar{2}\bar{1})$ gave values of $53^\circ 29'$, $53^\circ 30'$, $53^\circ 31'$, $53^\circ 6'$, $53^\circ 15'$, $53^\circ 41'$, averaging $53^\circ 22'$; hence the polar angle of $(20\bar{2}1)$ is $63^\circ 19'$. Two good measurements of the angle between $(10\bar{1}0)$ and $(10\bar{1}0)$ were $89^\circ 41'$ and $89^\circ 49'$, averaging $89^\circ 45'$. The twinning plane is therefore $10\bar{1}1$. The angles measured between the prisms were never over $30'$ from 60° .

The conditions of formation of the second crystal were similar to those of the first but the maximum temperature was about 100°* and the tube was allowed to stand at room tem-

* We do not know the inversion temperature of FeS with an excess of sulphur and can not, therefore, be certain that this and the following crystals were formed below that temperature. Their habit, however, is evidence that they belong to the low temperature form.

perature for about three months before opening. A considerable number of small, twinned crystals similar to the measured crystal and in no case over 0.15^{mm} in length were formed. The measured crystal was similar in its development to crystal 1, except that the pyramids were somewhat striated parallel to the base and $\{16.0.\bar{1}6.7\}$ was the dominant pyramid. The reflections were not quite so good as those of the first crystal. Six measurements of the polar angle of $(16.0.\bar{1}6.7)$ varied from $66^{\circ} 0'$ to $66^{\circ} 31'$, averaging $66^{\circ} 18'$. The signals for the face $(20\bar{2}1)$ did not stand out sharply from the other signals of its zone, but three measurements of the angle between the points where the strings of signals for the pyramid zones of the two individuals intersected gave $52^{\circ} 47'$, $53^{\circ} 32'$, and $52^{\circ} 34'$, averaging $52^{\circ} 58'$. The polar angle of $(20\bar{2}1)$ is, therefore, $63^{\circ} 31'$. One good measurement of the angle between the prism faces of the two individuals was $90^{\circ} 14'$. The angles in the prism zone may differ as much as $30'$ from 60° .

The third preparation was formed as was the second but the crystals differed in that the base was rather prominent and the form $\{50\bar{5}1\}$ was present. The habit of these crystals is shown in fig. 23. The measured crystal which was less than 0.2^{mm} in length gave rather poor signals, and many of the faces were very poor or missing. There was a continuous line of signals from the prisms to the pyramids $(20\bar{2}1)$ and the angle between the intersections of these zones belonging to the two individuals measured $52^{\circ} 34'$ and $52^{\circ} 0'$, averaging $52^{\circ} 20'$. Therefore the polar angle of $(20\bar{2}1)$ is $63^{\circ} 50'$. The angle between the bases of the two individuals measured $90^{\circ} 7'$. Three measurements of the polar angle of $(16.0.\bar{1}6.7)$ averaged $66^{\circ} 25'$ with a maximum deviation of $19'$. Five measurements of the polar angle of $\{50\bar{5}1\}$ averaged $78^{\circ} 55'$ with a maximum deviation of $26'$. The angles between the prisms could not be measured accurately but they differed from 60° by less than $20'$.

The data for the three measured crystals of β -pyrrhotite are assembled in Table XII. The table shows the principal interfacial angles as measured on each crystal and as computed from the average value of the constant p_o , the faces observed on each crystal and the value of the vertical axis c . There is a close agreement between the measured and the computed angles and it seems certain that the difference in the value of p_o for the different crystals represents an actual difference in the crystal constants. Their difference is easily accounted for, as the amount of sulphur in pyrrhotite varies considerably.

A comparison of the two forms of pyrrhotite.—The following criteria for distinguishing between the two forms of

pyrrhotite applied to all of the artificial crystals which were examined and should serve as more or less reliable means of distinguishing between the two forms in both natural and synthetic crystals:

1. The habit of β -pyrrhotite is hexagonal and the dominant forms are the prism, and a steep pyramid, and sometimes also the base (figs. 22 and 23). α -pyrrhotite, on the other hand, is always tabular parallel to the base; a few of the crystals appear to be hexagonal, but most of them are much elongated in the direction of the a axis and the orthorhombic symmetry is further shown by the common association of the forms $\{001\}$, $\{100\}$, and $\{111\}$ (figs. 17, 18 and 20).

2. The low temperature form (β) is almost invariably developed as cruciform twins with an angle of about 90° between the two individuals (twinning plane $10\bar{1}1$), while the high temperature form (α) is usually twinned after (023) with the two individuals at about 65° to each other, and sometimes also after (021) with the two individuals at about 55° to each other.

3. The constant p_0 for the measured crystals of β -pyrrhotite varied from 0.9967 to 1.0100, while for α -pyrrhotite it varied from 0.9267 to 0.9927. While crystals for which the value of p_0 was approximately 1.0000 were found in both

TABLE XII.

Crystal data of β -Pyrrhotite.

	Crystal 1		Crystal 2		Crystal 3	
	Observed	Computed $p_0=0.9967$	Observed	Computed $p_0=1.004$	Observed	Computed $p_0=1.01$
Polar angle of $(20\bar{2}1)$	$63^\circ 19'$	$63^\circ 19'$	$63^\circ 31'$	$63^\circ 32'$	$63^\circ 50'$	$63^\circ 40'$
Angle between twins	$89^\circ 45'$	$89^\circ 42'$	$90^\circ 14'$	$90^\circ 14'$	$90^\circ 7'$	$90^\circ 34'$
Polar angle of $(50\bar{5}1)$	----	----	----	----	$78^\circ 55'$	$78^\circ 48'$
Polar angle of $16.0.1\bar{6}.7$)	----	----	$66^\circ 18'$	$66^\circ 27'$	$66^\circ 25'$	$66^\circ 35'$
Faces	$(10\bar{1}0)$	$(20\bar{2}1)$	$(10\bar{1}0)$	$(20\bar{2}1)$ $(16.0.1\bar{6}.7)$	$(10\bar{1}0)$	$(20\bar{2}1)$ $(16.0.1\bar{6}.7)$ $(000\bar{1})$ $(50\bar{5}1)$
c	0.8632		0.8695		0.8742	

forms and the unknown limiting values would introduce a greater ambiguity, yet crystals for which p_o is considerably less than 1.0000 are likely to be α -pyrrhotite while those for which p_o is considerably greater than 1.000 are probably β -pyrrhotite.

Natural Pyrrhotite.

Pyrrhotite has generally been considered hexagonal, but as early as 1878 Streng* suggested that it was orthorhombic and isomorphous with sternbergite. However, in 1882 he† concluded that the mineral was hexagonal from a study of the crystal form, etch figures, heating curve, and magnetic properties. Vrba,‡ Frenzel,§ and Dom Pedro von Sachsen-Coburg|| measured crystals whose angles indicated orthorhombic symmetry. Crystals associated with limestone containing garnets are described by Roth¶ as elongated along a horizontal axis and hence orthorhombic in habit. Nicol** described crystals with a "decided orthorhombic appearance." Recently Weiss†† studied the magnetic properties of pyrrhotite and concluded that it was probably monoclinic but that it could not have a higher symmetry than orthorhombic. Kaiser‡‡ concluded, from a study of magnetic and other properties, that the mineral occurred in twinned orthorhombic crystals.

There has also been a lack of agreement in the measured angles and length of the vertical axis. Table XIII gives the important crystal data for the eleven measured crystals of natural pyrrhotite which seemed to be most reliable. The first column contains the name of the author; the second, the observed faces in the order of their prominence on the crystal giving the hexagonal symbol assigned by Dana; the third column gives the habit of the crystal; the fourth column, the most probable value of p_o . The occurrence and associated minerals are listed in the fifth column. The values for the constant p_o are reliable only for the crystals of Busz, Nicol, Seligmann, Kenngott, Rose, and perhaps Shephard. The crystal of D'Achiardi gave values of p_o ranging from 0.9658 to 1.0240 depending on which pyramid was used in the calculation. That of Dom Pedro gave no good measurements. The two crystals of Streng and the one of Dana afforded measurements on only one pyramid and the value of p_o depends upon the symbol assigned to it.

* Jahrb. Min., p. 797, 1878.

† Jahrb. Min., i, p. 183, 1882.

‡ Zs. Kryst. Min., iii, p. 190, 1879.

§ Min. Petr. Mitt., iii, 297, 1881.

|| Min. Petr. Mitt., x, 451, 1888.

¶ Z. Kryst. Min., ix, 309, 1884.

** Zs. Kryst. Min., xxxi, 53, 1899.

†† Jour. de Phys., pp. 469 and 829, 1905; Centralbl. Min., p. 338, 1906.

‡‡ Centralbl. Min., p. 261, 1906.

TABLE XIII. MEASURED CRYSTALS OF NATURAL PYRROTITE.

Author	Faces	Habit	p .	Occurrence and associations
1. Busz -----	(0001) (10 $\bar{1}$ 2) (10 $\bar{1}$ 0) (20 $\bar{2}$ 1)	Tabular (0001)	0.9407	Andreasburg. Crystals on calcite. Fontenac County, Canada. Calcite apatite, pyrite.
2. Nicol -----	(0001) (10 $\bar{1}$ 0) (20 $\bar{2}$ 1) (40 $\bar{4}$ 1) (10 $\bar{1}$ 1)	Decided rhombic appearance	0.946	
3. Seligman --	(0001) (10 $\bar{1}$ 0) (40 $\bar{4}$ 1) (10 $\bar{1}$ 1)	Tabular after (0001)	0.9528	Cyclopean Isle. In analcite basalt with molybdenite, etc.
4. Kengott ---	(0001) (10 $\bar{1}$ 0) (20 $\bar{2}$ 1)	-----	0.9995	Kongsberg, Norway.
5. Streng ----	(0001) (10 $\bar{1}$ 0) (20 $\bar{2}$ 1)	-----	1.1195 ?	Kongsberg, Norway.
6. D'Achiardi	(0001) (10 $\bar{1}$ 0) (20 $\bar{2}$ 1) (40 $\bar{4}$ 1) (60 $\bar{5}$ 1)	Tabular (0001)	1.000 \pm	Bottino. On argentiferous galena.
7. Rose -----	(20 $\bar{2}$ 1) (0001) (10 $\bar{1}$ 0)	-----	1.002	Meteorite. Augite and feldspar.
8. Shephard --	(12 $\bar{1}$ 0) (24 $\bar{2}$ 1) (10 $\bar{1}$ 1)	-----	1.0029	Meteorite.
9. Dana (E.S.)	(0001) (20 \cdot 0.50.3) ?, (0001)	Twinned after (10 $\bar{1}$ 1)	1.0035	Elizabethtown, Ontario. Pyrite, talc, calcite, plagioclase, etc. Magnetic poles at sides of crystals in (0001).
10. Dom Pedro Augusto von Sachsen Coburg	(0001) (10 $\bar{1}$ 0) (10 $\bar{1}$ 1) (40 $\bar{4}$ 1)	Tabular after (0001)	1.0412 \pm	Minas Geraes, Brazil. Gold vein with pyrite, arsenopyrite, chalcopyrite, albite, calcite, apatite, cronstedtite, scheelite, etc.
11. Streng ----	(10 $\bar{1}$ 0) (10 $\bar{1}$ 2)	-----	1.0972	Chanarcillo, Chile.

1. N. Jahrb. Min., i, 124, 1895.
2. Zs. Kryst. Min., xxxi, 53, 1899.
3. Zs. Kryst. Min., xi, 343, 1886.
4. Ber. Ak. Wien, ix, 575, 1852.
5. N. Jahrb. Min., 925, 1878.
6. Proc. Soc. Tosc. Sc. Nat. Pisa, xiii, 140, 1903.
7. Pogg. Ann., iv, 180, 1825.
8. This Journal, xvi, 201, 1829.
9. Ibid., xi, 386, 1876.
10. Min. Petr. Mitt., x, 451, 1888.
11. Loc. cit.

The results of the different investigations are brought into agreement by the recognition of the two forms of pyrrhotite and also of the change in p_o with a change in the composition of the mineral. The early view of Streng* that pyrrhotite is orthorhombic and belongs to the chalcocite group holds true for α -pyrrhotite, while β -pyrrhotite is hexagonal. Further investigation may show that other members of these groups are dimorphic.

A further study of Table XIII shows that most of the eleven crystals were probably formed as α -pyrrhotite. Crystals 1 to 3 have low values for p_o , tabular habits, and crystal 3, at least, has an association which would indicate the high temperature form. Crystal 2, in particular, is described as having a "decided orthorhombic appearance" and the orthorhombic axis is shown by the elongation along it and the development of the form $\{221\}$ but not $\{041\}$, and of $\{011\}$ but not $\{112\}$. Crystals 4 and 5 from Kongsberg might belong to either form, but their tabular habit suggests α -pyrrhotite. Crystal 6 has the tabular habit of α -pyrrhotite. Crystal 10 has a tabular habit and is, in addition, associated with minerals which indicate the high temperature form. The occurrence of crystals 7 and 8 in meteorites places them as α -pyrrhotite. The hexagonal development and the twinning of crystal 9 indicate β -pyrrhotite, but the association with feldspar, etc., and the position of the magnetic poles are not consistent with this view.

Any list of the faces which have been found on α -pyrrhotite will be somewhat uncertain since some of the measured crystals might belong to either form, and, besides, the variable character of p_o makes it impossible to assign a symbol to some of the measured pyramids. The following list omits doubtful faces and marks with a star those found only on synthetic crystals.

c (001)	f' (012)	j (061)	r (221)
b (010)	e (023)*	n (201)	s (331)
a (100)	g (011)	q (114)	u (623)
m (110)	h (021)	v (112)	
l (310)	i (041)	p (111)	

Summary.

1. The formation of iron disulphide was accomplished (1) by the action of hydrogen sulphide on ferric salts, or the action of sulphur and hydrogen sulphide on ferrous salts; (2) by the addition of sulphur from solution to amorphous ferrous sulphide or pyrrhotite; (3) by the action of soluble polysulphides

* Loc. cit.

on ferrous salts; (4) by the action of soluble thiosulphates on ferrous salts according to the equation $4M_2S_2O_3 + FeX_2 = 3M_2SO_4 + FeS_2 + 2MX + 3S$. The first three methods may be generalized as *the action of sulphur on ferrous sulphide*: (a) in acid solutions; (b) in nearly neutral solutions, and (c) in alkaline solutions, since in (1) we may assume that ferrous sulphide first forms by the action of hydrogen sulphide on the ferrous salt, and in (3) we know that polysulphides first precipitate a mixture of ferrous sulphide and sulphur. Marcasite was obtained with certainty only by method (1); low temperatures and free acid favor its formation. A solution containing about 1 per cent of free sulphuric acid at 100° gives pure marcasite. Less acid solutions at higher temperatures give mixtures of marcasite and pyrite. The other methods give pyrite which, under certain conditions, may be mixed with amorphous disulphide. It is possible that some marcasite may be formed by method (4).

2. Marcasite and pyrite were identified in the above products: (1) By microscopic examination and crystallographic measurement. The pyrite crystals showed only the cube and the octahedron. Marcasite crystals were formed for the first time. They were commonly twinned after (110), and their habits are shown in figures 15 and 16, Pt. III. The axial ratios of the synthetic mineral are $a:b:c = 0.7646:1:1.2176$ and agree remarkably well with those of the natural mineral. (2) By Stokes's oxidation method, which serves also for the analysis of mixtures of the two minerals.

3. Marcasite changes to pyrite with evolution of heat. The change proceeds very slowly at 450° and is not accelerated by pressures even of 10,000 atmospheres. Marcasite is monotropic toward pyrite. This is in accord with the greater inclination of marcasite to oxidize, its assumed greater solubility, and the fact that its formation is conditioned by the composition of the solution from which it crystallizes.

4. The fact that marcasite never occurs as a primary constituent of magmas, while pyrite sometimes does, is explained by the fact that marcasite cannot exist above 450° . The formation of pyrite in deep veins and hot springs is explained by the fact that the waters from which it came were alkaline. The marcasite of surface veins was probably formed from cold acid solutions, while mixtures of marcasite with pyrite were probably conditioned by higher temperature (up to 300°), or the presence of less acid, or both. Micro-organisms may have been active in the formation of pyrite and marcasite by giving rise to hydrogen sulphide.

5. Pyrrhotite was formed by the decomposition of pyrite or heated marcasite, or by heating iron with excess of sulphur.

The dissociation of pyrite into pyrrhotite and sulphur is readily reversible. At 565° (about) pyrite and pyrrhotite are in equilibrium with the partial pressure of sulphur in H_2S , which here amounts to about 5^{mm} (data of Preunner and Schupp); at 550° in hydrogen sulphide, the pyrrhotite passes into pyrite, and at 575° the reverse action proceeds. At about 665° the evolution of sulphur from pyrite becomes rapid and a marked absorption of heat results. The pressure of the sulphur vapor here probably reaches one atmosphere.

6. Pyrrhotite is of variable composition. Its composition at any temperature depends on the pressure of sulphur vapor in which it is heated. Though it has not been found feasible to vary the temperature and pressure independently, a series of products were prepared by first decomposing pyrite and then reheating the resulting material to various measured temperatures in hydrogen sulphide and finally chilling in the same or cooling in nitrogen. The products lowest in sulphur were obtained in the latter way. These products all resemble natural pyrrhotite in physical and chemical properties. Their specific volumes vary continuously with composition and pyrrhotite is therefore to be regarded as a solid solution of sulphur in ferrous sulphide. The maximum percentage of dissolved sulphur in synthetic pyrrhotite was 6.04 per cent at 600° . By extrapolation the saturated solution at 565° , below which point pyrite forms, was estimated to be 6.5 per cent. This corresponds closely to the maximum percentage of sulphur reported in natural pyrrhotite.

7. Equilibria between pyrrhotite and the partial pressure of sulphur in dissociated hydrogen sulphide were determined at different temperatures, by sufficiently long heating and then rapid cooling. The dissolved sulphur varied under these conditions from 6.0 per cent at 600° to 2.0 per cent at 1300° . The curve shows a discontinuity at the melting temperature, at the beginning of which there is a sudden decrease in the percentage of sulphur.

8. The melting point of pure ferrous sulphide could not be exactly determined because the compound dissociates at high temperatures into its elements. By heating it in a vacuum this dissociation was placed beyond doubt, though the dissociation was so slow that the melting point could be located approximately. It may safely be put at $1170^{\circ} \pm 5^{\circ}$. In hydrogen sulphide, the melting temperature is raised, because the solid solution thus formed contains more sulphur than the first portion of liquid to which it melts. The limits of the melting interval cannot be determined as yet, but the maximum heat absorption falls at 1183° . In one atmosphere of sulphur vapor this temperature rises to 1187° .

9. Crystals of pyrrhotite, the measurements of which are recorded under the Crystallographic Study, were repeatedly formed at various temperatures between 80° and 225° by the action of hydrogen sulphide on slightly acid solutions of ferrous salt containing some ferric salt. The product usually contained some crystals of disulphide.

10. The crystallographic study confirms the work of Rinne and Boeke and others, that there are two crystal forms of pyrrhotite. The high temperature form, α -pyrrhotite, appears to be orthorhombic and the axial ratios vary from $a:b:c = 0.5793:1:0.9267$ to $0.5793:1:0.9927$, depending on the amount of the dissolved sulphur present (?). The habits of the crystals are shown in figs. 17, 18 and 20, Pt. III. β -pyrrhotite is hexagonal, and c varies from 0.8632 to 0.8742. The crystal habit is shown in figs. 22 and 23, Pt. III.

The crystal constants of natural pyrrhotite can not be assumed to be invariable, since the composition of the mineral is not constant, and the crystal angles of the synthetic mineral are variable. The lack of agreement among mineralogists regarding the crystal system to which pyrrhotite belongs can be explained on the theory that there are two forms of pyrrhotite.

11. Troilite is only the end member of the pyrrhotite series and not a distinct mineral species. Thus far, it has not been prepared free from metallic iron.

In conclusion, the authors wish to express their hearty thanks to Dr. Carl Alsberg and Dr. Oswald Schreiner for important references, and to Dr. F. L. Ransome, Dr. W. H. Emmons and Mr. C. A. Davis for valuable geological information, and especially to Mr. W. Lindgren, not only for placing at our disposal the generalized results of his extensive experience, but for reading this paper and making a number of important suggestions.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., Dec. 1, 1911.

